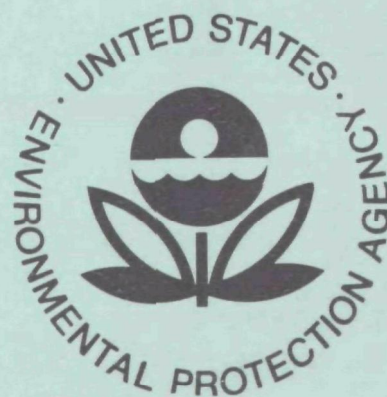


EPA-600/3-76-107  
November 1976

Ecological Research Series

# OXIDANT-PRECURSOR RELATIONSHIPS DURING POLLUTANT TRANSPORT CONDITIONS

## An Outdoor Smog Chamber Study



Environmental Sciences Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, North Carolina 27711

## **RESEARCH REPORTING SERIES**

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ECOLOGICAL RESEARCH series. This series describes research on the effects of pollution on humans, plant and animal species, and materials. Problems are assessed for their long- and short-term influences. Investigations include formation, transport, and pathway studies to determine the fate of pollutants and their effects. This work provides the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic, terrestrial, and atmospheric environments.

EPA-600/3-76-107  
November 1976

OXIDANT-PRECURSOR RELATIONSHIPS DURING  
POLLUTANT TRANSPORT CONDITIONS  
An Outdoor Smog Chamber Study

by

L. A. Ripperton, J. E. Sickles, II, and W. C. Eaton  
Systems and Measurements Division  
Research Triangle Institute  
Research Triangle Park, North Carolina 27709

Contract No. 68-02-1296

Project Officer

J. J. Bufalini  
Gas Kinetics and Photochemistry Branch  
Environmental Sciences Research Laboratory  
Research Triangle Park, North Carolina 27711

Environmental Sciences Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, North Carolina 27711

## DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## ABSTRACT

The formation of ozone under simulated conditions of pollutant transport was studied in a group of four 27-cubic-meter outdoor smog chambers. The chambers were constructed of 5 mil FEP Teflon on aluminum frames. The initial charges in the smog chambers were irradiated for three days by natural sunlight. Simulation of transport was accomplished by progressively diluting the contents of the chambers with clean air.

The analogy between the chemical behavior of chamber simulations and nonurban high-ozone (i.e., 0.08 ppm) systems in the field was good. On the second and third days, the initial charges in the chambers generated ozone concentrations greater than the National Ambient Air Quality Standard for photochemical oxidant (0.08 ppm).

The initial charge of nonmethane hydrocarbon (NMHC) ranged from 1.0 to 10.0 ppmC; nitrogen oxides ( $\text{NO}_x$ ) ranged from 0.100 to 1.000 ppm. Therefore, initial ratios of NMHC/ $\text{NO}_x$  varied from 7 to 20. On the second and third days in the chambers, concentrations of  $\text{NO}_x$  ranged from 0.001 to 0.053 ppm; NMHC ranged from 0.33 to 3.78 ppmC. The resulting NMHC/ $\text{NO}_x$  ratios varied from 16 to 610.

This report was submitted in fulfillment of EPA contract 68-02-1296 (43U-994, RTI Contract Number) by the Research Triangle Institute under the sponsorship of the Environmental Protection Agency.



## CONTENTS

Abstract . . . . .	iii
Figures . . . . .	vi
Tables . . . . .	vii
I. Introduction . . . . .	1
II. Conclusions . . . . .	2
III. Recommendations . . . . .	4
IV. Description of RTI Smog Chamber Facility . . . . .	8
Design . . . . .	8
Characterization . . . . .	15
V. Design of Study . . . . .	17
Research plan . . . . .	17
Reagents . . . . .	20
Measurement methods . . . . .	21
VI. Discussion of Results . . . . .	23
Ozone precursor relationships . . . . .	25
"Fossil" ozone . . . . .	40
Dilution effect . . . . .	45
Comparison of field observations with smog chamber results . . . . .	48
References . . . . .	56
Appendixes . . . . .	57
A. Individual hydrocarbon analyses . . . . .	57
B. Concentration profiles . . . . .	78

## FIGURES

<u>Number</u>		<u>Page</u>
1	A 27-cubic meter Teflon outdoor smog chamber . . . . .	9
2	System diagram, RTI smog chambers . . . . .	10
3	Air purification unit, RTI smog chamber . . . . .	11
4	Reactant injection system, RTI smog chambers. . . . .	13
5	Sampling system, RTI smog chambers. . . . .	14
6	Range of all possible combinations of NO <sub>x</sub> and nonmethane hydrocarbon concentrations used in experimental work . . . .	19
7	Average maxima, minima, and ΔO <sub>3</sub> concentrations as a function of NO <sub>x</sub> concentrations at sunrise on the second and third days <sup>x</sup> of irradiation. . . . .	36
8	Average maxima, minima, and ΔO <sub>3</sub> concentrations as a function of nonmethane hydrocarbon concentrations on the second and third days of irradiation. . . . .	37
9	Average maxima and ΔO <sub>3</sub> as a function of nonmethane hydro- carbon to oxides of nitrogen ratio . . . . .	39
10	Vertical ozone soundings, August 1, 1974, Wilmington, Ohio. . .	41
11	Ozone profiles over second-day irradiations for same initial conditions and different dilutions in Chamber #1 . .	46
12	Mean diurnal O <sub>3</sub> concentration at Wilmington, Wooster, and McConnelssville, Ohio, from June 14-August 31, 1974 . . . . .	49
13	Mean diurnal NO <sub>2</sub> concentration at Wilmington, Wooster, and McConnelssville, Ohio, from June 14-August 31, 1974 . . . . .	50
14	Mean diurnal NMHC concentration at Wilmington, Wooster, and McConnelssville, Ohio, from June 14-August 31, 1974 . . . . .	51
15	Typical three-day profiles for NO (□), NO <sub>2</sub> (Δ), and O <sub>3</sub> (x). . .	52



## TABLES

<u>Number</u>		<u>Page</u>
1	Initial Reactant Concentrations for a Proposed Extension of the Study of Ozone-Precursor Relationships Under Conditions of Pollutant Transport . . . . .	5
2	Dilution Rate (24-Hour Dilution) . . . . .	17
3	Selected Experimental Conditions, Contract (68-02-1296) . . .	18
4	Experimental Conditions, Extended Project . . . . .	18
5	Selected Results from the July 17-18 Two-Day Chamber Runs . . . . .	26
6	Selected Results from the July 22-24 Three-Day Runs . . . . .	27
7	Selected Results from the July 28-30 Three-Day Runs . . . . .	28
8	Selected Results from the August 4-6 Three-Day Runs . . . . .	29
9	Selected Results from the August 8-10 Three-Day Runs . . . . .	30
10	Selected Results from the August 12-14 Three-Day Runs . . . . .	31
11	Net Ozone Generated on Second and Third Days of Irradiation as a Function of Oxides of Nitrogen and Nonmethane Hydrocarbon/Oxides of Nitrogen Ratio . . . . .	32
12	Maximum Ozone Concentration on Second and Third Days of Irradiation as a Function of Oxides of Nitrogen and Nonmethane Hydrocarbon/Oxides of Nitrogen Ratio. . . . .	33
13	Net Ozone Generated on Second and Third Days of Irradiation as a Function of Nonmethane Hydrocarbon and Nonmethane Hydrocarbon/Oxides of Nitrogen Ratio . . . . .	34
14	Maximum Ozone Concentration on Second and Third Days of Irradiation as a Function of Nonmethane Hydrocarbon and Nonmethane Hydrocarbon/Oxides of Nitrogen Ratio. . . . .	35
15	Dark-Phase Ozone Half-Lives in Smog Chamber Runs. . . . .	43

## SECTION I

### INTRODUCTION

In the troposphere the primary pollutants, nitrogen oxides and hydrocarbons, in the presence of sunlight can serve as ozone precursors. Definition of the influence of various environmental factors (such as transport) on ozone formation is important in the design of strategies to prevent the occurrence of excessive ozone concentrations.

Studies of experimentally produced photochemical smog have been mainly concerned with simulation of "downtown" urban atmospheric conditions. Typically, most experiments have involved from two to six hours of irradiation. Recently observed high nonurban ozone concentrations (greater than 0.08 ppm hourly average) have called attention to the need to study the oxidant/oxidant-precursor relationships in pollution systems after they leave the city (i.e., leave the major sources of pollution). Under these conditions, the pollution system is irradiated for prolonged periods (perhaps for several diurnal cycles) with sunlight and is diluted with nonurban air.

A study designed to investigate this problem should:

1. Determine the influence of oxides of nitrogen/hydrocarbon ratios ( $\text{NO}_x/\text{HC}$ ) upon oxidant generation under various conditions of transport (as simulated by different dilution regimes).
2. Determine the potential for oxidant production of  $\text{NO}_x/\text{HC}$  mixtures in the course of several diurnal cycles of irradiation.

The objective of this study is to investigate, in outdoor reaction chambers, the oxidant/ $\text{HC}/\text{NO}_x$  relationships in air mixtures that are similar to those resulting from drift of air pollution systems from urban environs. Specifically, the oxidant/ $\text{HC}/\text{NO}_x$  relationships will be examined under chamber-simulated conditions of atmospheric dilution and repeated diurnal solar irradiation. The study is designed to address the question of the maximum oxidant concentration obtainable from a given initial concentration of precursors on both the initial day of solar irradiation and on subsequent days of irradiation.

## SECTION II

### CONCLUSIONS

A study was designed to simulate the effects of transport of oxidant and oxidant precursors on ozone ( $O_3$ ) concentration behavior downwind from urban areas. To perform this simulation, experimental urban photochemical systems were irradiated for three daylight periods with natural sunlight. In most cases, there was a period of dilution of the reactant system to simulate the dilution of urban pollution downwind of the center city. A system of four 27-cubic-meter (950 cubic feet) outdoor smog chambers was used for irradiation of the pollutants. The chambers were fabricated of an aluminum frame covered with Teflon film.

The initial charges consisted of a mixture of hydrocarbons and oxides of nitrogen ( $NO_x$ ) (20% nitrogen dioxide) in ratios of 7 to 20 and absolute concentrations of 1 to 10 ppmC nonmethane hydrocarbon (NMHC) and 0.100 to 1.000 ppm  $NO_x$ . By the second and third day, the measured NMHC concentration range was 0.33 to 3.78 ppmC and the measured  $NO_x$  was 0.001 to 0.053 ppm.

The second and third day behavior of  $O_3$  concentrations was remarkably similar to that observed in the field by RTI in rural areas which exceeded the National Ambient Air Quality Standard (NAAQS) for photochemical oxidant.

The conclusions drawn from the study are presented below. 1) Oxides of nitrogen in the 1-5 ppb concentration range (the noise level of current instrumentation) are capable of generating net concentrations of  $O_3$  in excess of the NAAQS in aged photochemical pollution systems; 2) Nonmethane hydrocarbon (largely "nonreactive") concentrations only slightly higher than the NAAQS for NMHC (0.24 ppmC) are capable of generating net concentrations of  $O_3$  in excess of the NAAQS for photochemical oxidant; 3) Although the NMHC concentrations are greater than the NMHC NAAQS, this study suggests the possibility that in the downwind drift of the urban plume the current NMHC standard is ineffective to contain the  $O_3$  concentrations below the oxidant standard; 4) The  $O_3$ -precursor relationship as indicated by various graphs in the criteria document (ref. 1) do not seem applicable to the second- and third-day irradiation chamber results; 5) Within the chambers

aged photochemical systems after a day or two of solar irradiation maintained both  $O_3$ -destructive and  $O_3$ -generative capacity. This indicates that neither "fossil"  $O_3$  nor local precursor emissions are necessary to produce the  $O_3$  behavior observed in rural high  $O_3$  systems. When "fossil"  $O_3$  and local emissions are present, however, they do influence the nonurban high  $O_3$  systems; 6) "Fossil"  $O_3$  (i.e.,  $O_3$  generated in urban areas and retained in air moving downwind from a city) can account for the overnight retention of  $O_3$  concentrations above the NAAQS, but "fossil"  $O_3$  from an urban area cannot be maintained for several days at high concentrations under field conditions without augmenting daytime synthesis; 7) Dilution of a photochemical system producing  $O_3$  does not reduce the maximum  $O_3$  nor the net  $O_3$  concentration in direct proportion to the extent of dilution. At times, the net  $O_3$  generated is greater in the diluted system as compared to an undiluted system, although the maximum may be lower.

### SECTION III

#### RECOMMENDATIONS

Some current problems confronting the planners of oxidant control strategy which can be addressed with smog chamber studies are:

1. Will the achievement of the current NMHC standard in urban areas control  $O_3$  concentrations downwind from the cities?
2. Must one consider total NMHC or only the "reactive" hydrocarbons (e.g., alkenes) to achieve the oxidant standard in nonurban areas?
3. What is the effect of urban pollution on  $O_3$  concentrations in nonurban areas?
4. Given an urban situation in which NMHC is controlled (NMHC NAAQS  $\sim 0.24$  ppm) and  $NO_x$  remains uncontrolled (e.g.,  $NO_x \sim 0.500$  ppm), is there danger of  $O_3$  levels' rising above the NAAQS in areas downwind which have suburban or natural emissions of NMHC and  $NO_x$ ?
5. What is the  $O_3$ -generative capacity of systems containing various NMHC and  $NO_x$  concentrations in cold weather (e.g.,  $4.5^\circ C$ ), especially with multiple-day solar irradiation?

To answer question 1 above, smog chamber studies should extend the range of the initial reactant concentrations to lower levels than are usually employed and react for a 60-hour or greater period.

For example, a study with initial NMHC concentrations of 0.50, 0.25 and 0.10 ppmC (urban mix) would bracket the NAAQS for NMHC. Oxides of nitrogen concentrations of 0.005, 0.010, 0.050, and 0.100 ppm would provide a reasonable range of urban  $NO_x$  levels. The initial NMHC/ $NO_x$  ratio would be in the range of 1 to 100 (see table 1).

Different dilution rates can be employed to simulate transport of the system out of an urban area. Throughputs,  $(\frac{f}{V}t)$ , of 0.0, 1.5, and 3.0 in 24 hours will leave  $\sim 100\%$ , 23%, and 5% of the original system after dilution. A study with 3 NMHC concentrations, 4  $NO_x$  concentrations, and 3 dilution regimes would provide 36 sets of conditions.

Based on the suggested dilutions and on observations of runs made at concentrations of reactants higher than those listed above, it is evident

Table 1. Initial Reactant Concentrations for a Proposed Extension of the Study of Ozone-Precursor Relationships Under Conditions of Pollutant Transport

<div> <div>NO<sub>x</sub> ppm</div> <div>NMHC ppmC</div> </div>	.10	.25	.50
.005	20	50	100
.010	10	25	50
.050	2	5	10
.100	1	2.5	5

(NMHC/NO<sub>x</sub> ratios in the matrix)

that NMHC concentrations on the 2nd and 3rd day would be well below the NAAQS. The downwind urban effects would be well simulated--assuming no additional pollution is added once the air leaves the city.

Question 2 above considers the efficacy of controlling only "reactive" urban hydrocarbons (alkenes) to control oxidant downwind of the city. If one choses conditions using an urban hydrocarbon mix, which upon irradiation bracket the photochemical oxidant NAAQS on the second and third days of the run, the same run could be made with representative alkanes and aromatics instead of the urban hydrocarbon mix. Both single compounds (e.g., isopentane) and a surrogate rural mix (e.g., with 2 or 3% olefins) could be used.

A set of 3 series of experiments could be run to address this problem. Three NMHC concentrations (e.g., 0.5, 0.25, 0.05 ppmC), three NO<sub>x</sub> concentrations (e.g., 0.100, 0.050, 0.010 ppm), and three hydrocarbon types (urban mix with alkenes, rural mix, and isopentane) would make a study with 27 sets of conditions. This should answer the question of whether only the reactive hydrocarbons need be controlled to protect areas downwind of the cities from O<sub>3</sub> concentrations above the NAAQS.

Question 3 is basically a question of how urban pollution affects the  $O_3$  concentrations in suburban and rural areas which have some hydrocarbon and  $NO_x$  emissions of their own.

Nonmethane hydrocarbon,  $NO_x$ , and dilution regimes can be chosen to bracket  $O_3$  production of 0.080 ppm. When dilution begins, a mixture of NMHC and  $NO_x$  representative of suburban, small town, or natural conditions can be used as dilution air.

Question 4 is one which has arisen in Los Angeles. Hydrocarbon control without  $NO_x$  control has at times resulted in low  $O_3$  concentrations, but with  $NO_2$  concentrations in the middle of the day in the tenths of parts per million range (e.g., 0.500 ppm). A question which arises is what occurs when the urban  $NO_x$  is diluted to much lower concentrations with air containing suburban and natural hydrocarbons?

Sets of conditions can be determined in which high concentrations of  $NO_x$  (e.g., 0.500 - 1.000 ppm) and low concentrations of NMHC generate no  $O_3$  or only that necessary to satisfy the so-called photostationary condition.

Dilution during irradiation of this system with diluent air containing 0.100 to 0.500 ppm NMHC should put this problem in perspective. Theoretical considerations and practical experience can be used to predict in general terms how the  $O_3$  generation in these systems will behave. The described condition represents a real case, however, and real data from smog chamber runs should answer the question of the desirability of controlling hydrocarbons while leaving  $NO_x$  completely uncontrolled.

Question 5 addresses the question of reported winter concentrations of  $O_3$  in excess of the NAAQS in areas north of the Gulf Coast states. The approach to this problem is simple.

Long-range weather forecasts can be consulted to estimate arrival and duration of cold weather ( $4.5^\circ C$ ) and sunshiny skies. Outdoor smog chamber experiments can then be initiated.

Concentrations of NMHC and  $NO_x$  representative of urban areas can be introduced into the chambers and irradiated both statically and in a dilution mode for a series of 3 to 5 sunlight periods.

Initial hydrocarbons could be 0.5, 1.0, and 3.0 ppmC while  $NO_x$  concentrations of 0.05, 0.10, and 1.00 could be used. A smog chamber run would represent irradiation of such precursor systems in the cold for several days aloft, away from fresh pollution.

Chamber work is needed to address the problems associated with determining the minimum  $\text{NO}_x$  which will generate  $\text{O}_3$  in concentrations which are at or over the NAAQS, and the circumstances under which this minimum  $\text{NO}_x$  concentration will produce such high  $\text{O}_3$  concentrations. Related is the determination of circumstances under which  $\text{NO}_x$  or NMHC concentrations are controlling the maximum  $\text{O}_3$  accumulation.

To some extent, the studies suggested above will provide information on the problems mentioned in the preceding paragraph. It is felt that the problems of determining the minimum  $\text{NO}_x$  and NMHC concentrations which can generate  $\text{O}_3$  levels in excess of 0.08 ppm would best be approached at this time by studies similar to those recommended for questions 1 through 5 above.



## SECTION IV

### DESCRIPTION OF RTI SMOG CHAMBER FACILITY

#### DESIGN

The Research Triangle Institute has constructed four smog chambers (volume:  $27 \text{ m}^3$ ; surface to volume ratio:  $1.9 \text{ m}^{-1}$ ). Figure 1 illustrates the general design. The chambers were built out-of-doors and irradiation is provided by natural sunlight. The walls are 5-mil FEP Teflon film supported by aluminum frames. The floors are 10-mil FEP Teflon film laid over a reflective material (aluminum foil) which serves to raise the light intensity within the chambers and thus compensate for transmission losses through the walls.

Mixing in each chamber is provided by an 0.45-m aluminum fan blade driven by a 185-W motor using a belt-pulley system. Air velocity measurements were made within each chamber. The minimum air velocity was measured to be greater than  $0.05 \text{ m sec}^{-1}$  within 0.02 m of the floor. Air velocities increased with distance from the walls to a maximum value in excess of  $4.0 \text{ m sec}^{-1}$  near the moving fan blade.

In addition to the chambers proper, provisions were made for:

1. Ambient air intake purification
2. Reactant injection
3. Instrumented gas analysis
4. Wet chemical gas analysis

A line drawing illustrating the overall system is provided in Figure 2.

The details of the air purification unit are shown in Figure 3. This unit provides for the normal modes of chamber operation: purge, cleanup, and dilution.

During the purge mode, air is supplied by a blower from a 10-m meteorological tower. This air is then drawn through each chamber and exhausted at flow rates up to  $0.34 \text{ m}^3 \text{ min}^{-1}$  by three two-stage diaphragm pumps. Purging may also be accomplished at higher flow rates up to  $2.3 \text{ m}^3 \text{ min}^{-1}$  by opening a manway in the floor and allowing the tower blower to force air through each chamber.

After completion of the purge, the chambers are closed and air is recirculated through the purification unit. The purification unit contains the following equipment:

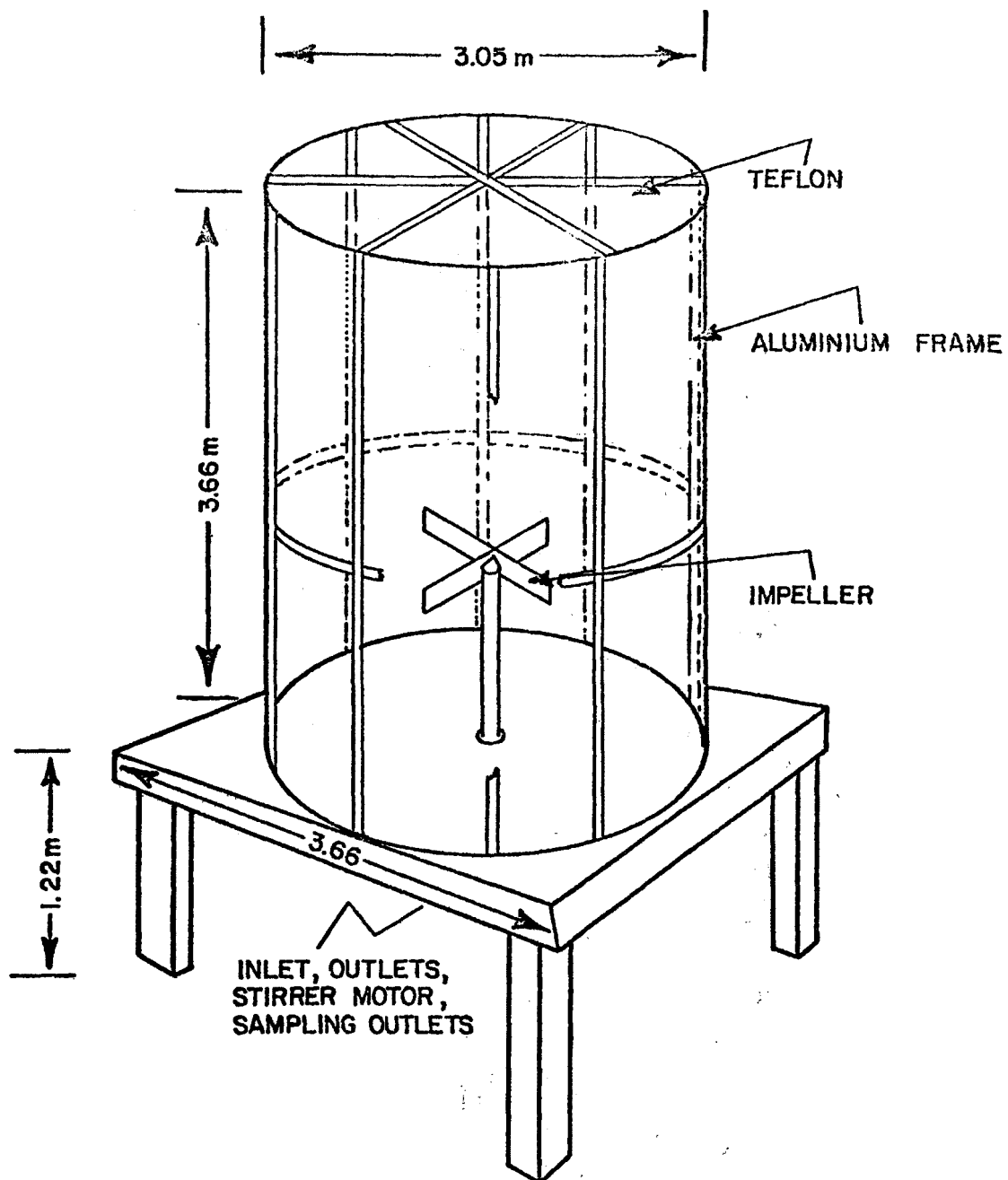


Figure 1. A 27-cubic meter Teflon outdoor smog chamber.

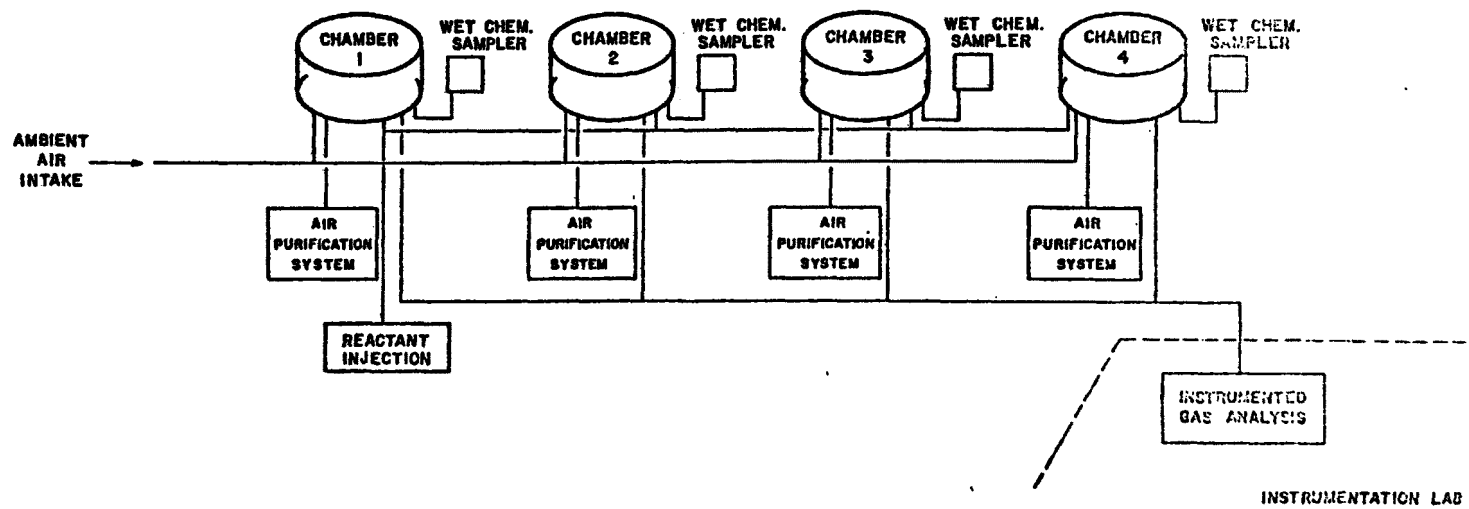


Figure 2. System diagram, RTI smog chambers.

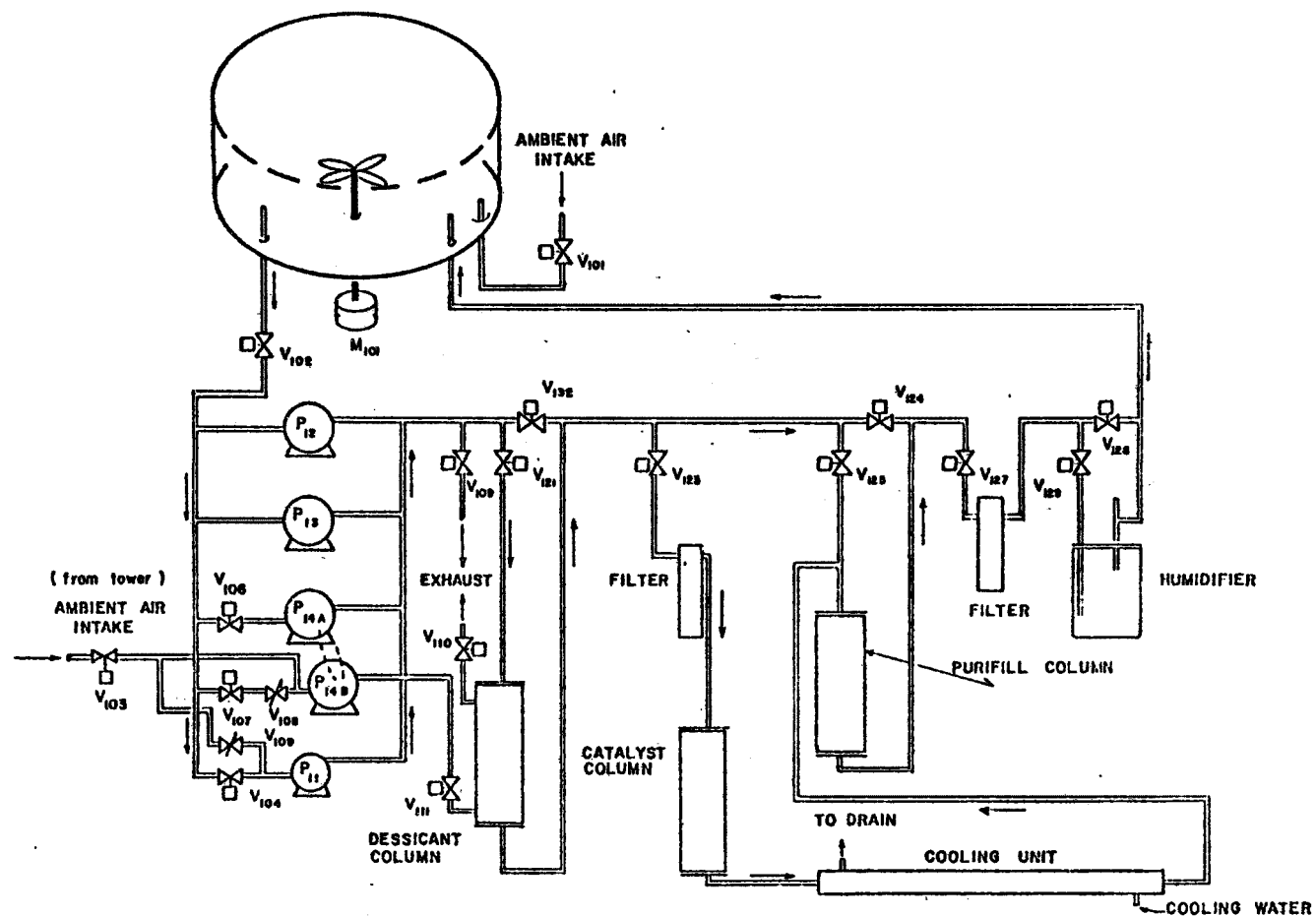


Figure 3. Air purification unit, RTI smog chamber.

1. Desiccant column (4A molecular sieves)
2. Two HEPA particle filters
3. Heated catalyst column (0.5% Pt on alumina catalyst; operating temperature: 200-475°C)
4. Air cooler
5. Purafil<sup>TM</sup> column (for NO<sub>x</sub> and O<sub>3</sub> removal)
6. Humidifier

Valving allows the inclusion or exclusion of this equipment as may be appropriate in achieving desired experimental conditions. The purification or "cleanup" operation requires 8 to 12 hours at a flow rate of approximately  $0.28 \text{ m}^3 \text{ min}^{-1}$ .

To effect dilution, the chamber contents are recirculated through the purification unit at appropriate flow rates to correspond to the desired dilution rate. Flow rates for this operational mode are between 0.0085 and  $0.085 \text{ m}^3 \text{ min}^{-1}$ .

A schematic of the reactant injection system is seen in Figure 4. There are three injection manifolds from cylinders of compressed gases. The flow rates are controlled by calibrated manual needle valves and the quantity of each injection is controlled by timed, manual operation of the appropriate solenoid valves. Hydrocarbons and carbon monoxide are injected sequentially from a single manifold as are NO and NO<sub>2</sub>. These manifolds are flushed to ambient between injections by compressed nitrogen. Ozone may be added by injecting oxygen through an O<sub>3</sub> generator to each chamber. A sketch of the sampling system is provided in Figure 5. The samples are drawn sequentially for 10-minute intervals through 0.0048-m ID TFE Teflon<sup>TM</sup> sample line. An automatic timer activates the appropriate sampling solenoid valves and provides for a 10-minute sample from each chamber once per hour. The remaining 20 minutes are used for instrument calibration or sampling from the ambient air supplied from the tower blower. The sample is drawn at approximately  $0.004 \text{ m}^3 \text{ min}^{-1}$  by a Metal-Bellows pump and is supplied to a glass manifold from which the instruments take their samples. These instruments include an O<sub>3</sub> analyzer, a NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer, an environmental chromatograph, and a dew point sensor. A 1-m-long, 0.0048-m ID TFE Teflon<sup>TM</sup> tube is located under each chamber. Wet bubbler sampler, condensation nuclei measurements, and bag samples (for detailed HC gas chromatographic analyses) are taken at this location.

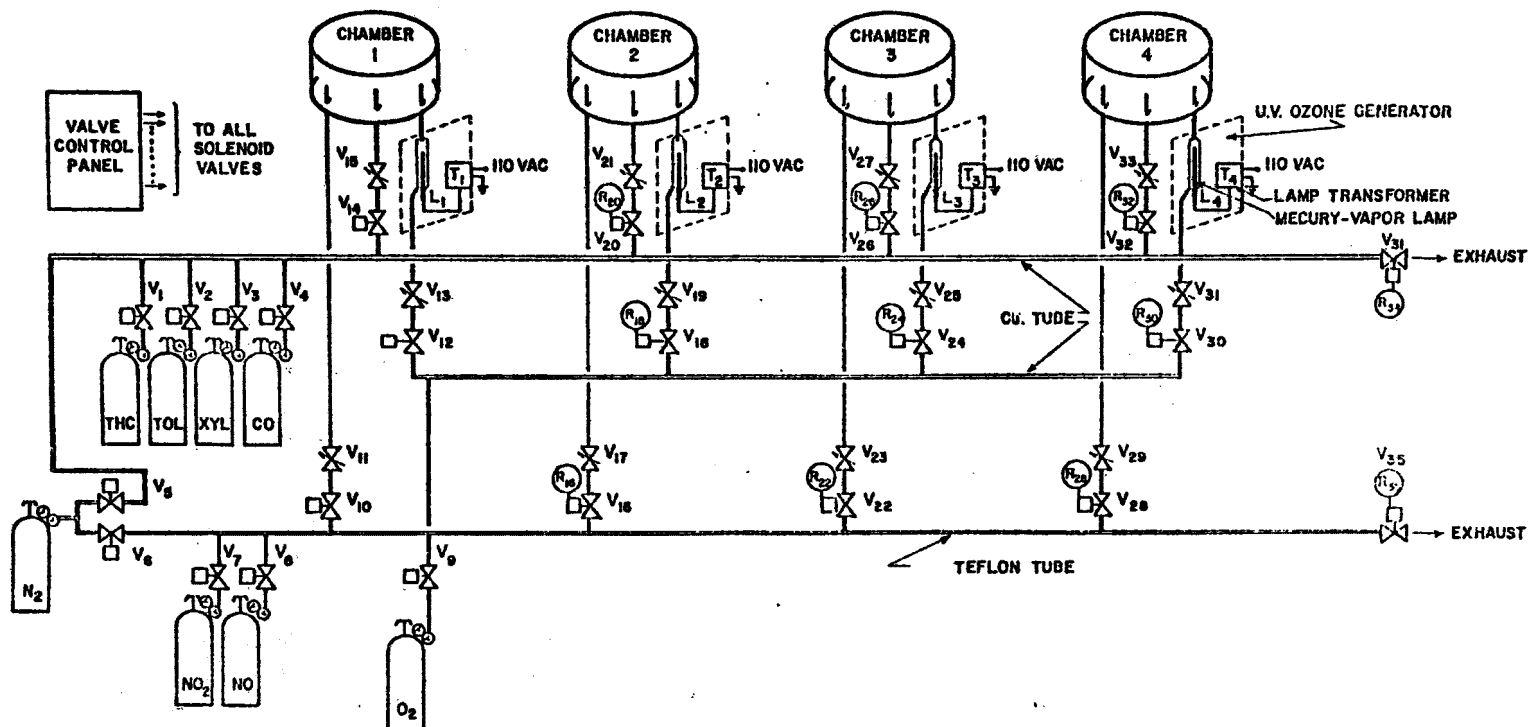


Figure 4. Reactant injection system, RTI smog chambers.

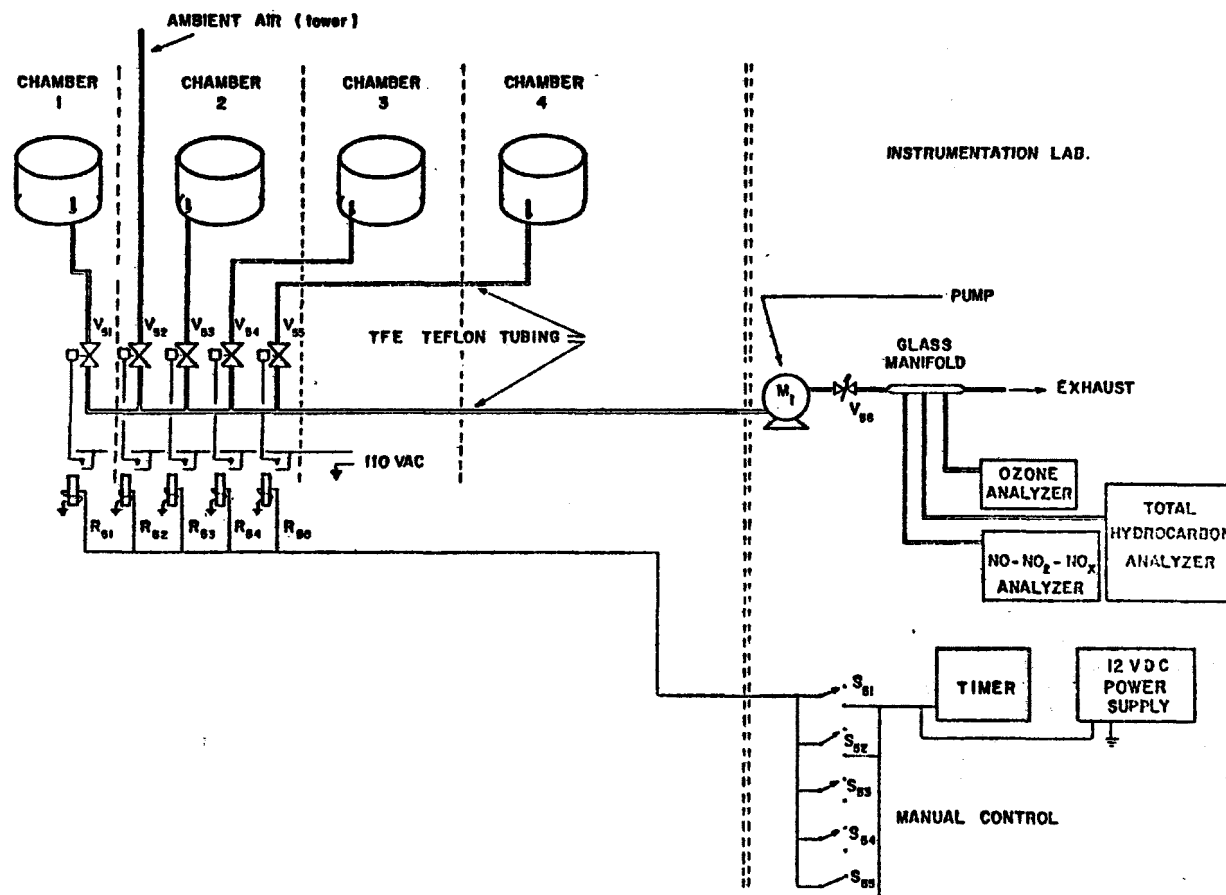


Figure 5. Sampling system, RTI smog chambers.

## CHARACTERIZATION

### Sample Line

At all concentrations examined, there is a 20% loss of  $O_3$  between the chamber and the  $O_3$  instrument. All quoted  $O_3$  concentrations have been corrected.

### The Cleanup System

The air cleanup system routinely reduces the  $NO_x$  content of make-up air to a measured zero. The catalyst beds, as constructed, are capable of reducing nonmethane hydrocarbon (NMHC) to 0.01 ppmC. Electrical and thermal problems, however, sometimes result in a decrease of the NMHC concentration to only 0.50 ppmC. These problems are (at this writing) being eliminated.

### Ozone Decay (8-1-75)

Dark phase [ $O_3$  concentration ~0.85 ppm]:

Chamber #1	$t_{1/2}$	~22 hours
Chamber #2	$t_{1/2}$	~27 hours
Chamber #3	$t_{1/2}$	~23 hours
Chamber #4	$t_{1/2}$	~30 hours

Light phase [ $O_3$  concentration ~0.45 ppm]:

Chamber #1	$t_{1/2}$	~10 hours
Chamber #2	$t_{1/2}$	~10 hours
Chamber #3	$t_{1/2}$	~11 hours
Chamber #4	$t_{1/2}$	~10 hours

### Nitric Oxide Oxidation (7-11-75)

Sunrise to 1400 hrs [NO concentration ~0.55 ppm]:

Chamber #1	.011 ppm hr <sup>-1</sup>	~ 2.5 × thermal
Chamber #2	.005 ppm hr <sup>-1</sup>	~1 × thermal
Chamber #3	.011 ppm hr <sup>-1</sup>	~2 × thermal
Chamber #4	.009 ppm hr <sup>-1</sup>	~2 × thermal

The THC reading during the above experiments were:

Chamber #1	0.05 ppmC
Chamber #2	0.13 ppmC
Chamber #3	0.02 ppmC
Chamber #4	0.07 ppmC



### Clean Air Irradiation (7-10-75)

The air in the chambers was cleaned and irradiation was started at sunup (ca. 0530 EDT). The O<sub>3</sub> maxima occurred in the 1600-1700 sampling period.

<u>Chamber #1</u>	<u>NMHC</u>	<u>NO<sub>x</sub></u>	<u>O<sub>3</sub> Max 1600-1700</u>
Chamber #1	~0.10 ppmC	tr (<1 ppb)	0.15 ppm
Chamber #2	~0.04 ppmC	tr (~2 ppb)	0.14 ppm
Chamber #3	~0.16 ppmC	tr (<1 ppb)	0.15 ppm
Chamber #4	~0.24 ppmC	tr (<1 ppb)	0.16 ppm

### Propylene-NO<sub>x</sub> Irradiation (7-9-75)

Simultaneous propylene-NO<sub>x</sub> runs were made with an approximate NMHC concentration of 1.20 ppmC and 0.35 ppm NO<sub>x</sub> (10% NO<sub>2</sub>).

#### Organics (ppmC)

<u>Chamber</u>	<u>Background After Cleanup NMHC</u>	<u>Propylene</u>	<u>Total NMHC</u>	<u>NO<sub>x</sub> ppm (10% NO<sub>2</sub>)</u>	<u>O<sub>3</sub> Max ppm</u>
Chamber #1	0.35	0.69	1.04	0.35	0.61 ppm
Chamber #2	0.45	0.82	1.27	0.36	0.70 ppm
Chamber #3	0.40	0.77	1.17	0.35	0.62 ppm
Chamber #4	0.42	0.93	1.35	0.38	0.71 ppm

#### Time NO<sub>x</sub> Crossover

Chamber #1	0933
Chamber #2	0927
Chamber #3	0924
Chamber #4	0857

Ozone maxima occurred between 1500 and 1540 (EDT).

## SECTION V

### DESIGN OF STUDY

#### RESEARCH PLAN

The original contract (EPA 68-02-1296) called for a series of experimental runs with 18 sets of conditions plus 6 replications. In subsequent talks with Dr. Basil Dimitriadis, a program involving 37 sets of experimental conditions plus 7 replications (44 experimental runs) was discussed. Twenty of the 37 sets plus 4 replications were run for purposes of this contract (EPA 68-02-1296) and the remainder are being run as part of the subsequent contract (EPA 68-02-2207). Dilution rates are shown in Table 2. Before dilution was initiated, the chambers were operated in the batch mode. The dilution was initiated at the time designated in Table 3, and dilution continued for 24 hours. After 24 hours, dilution was terminated and the chambers were operated again in the batch mode.

The conditions for the extended project are put forth in Table 4. The conditions for the 20 sets of conditions accomplished for this contract are set forth in Table 3.

The concentrations ranges are:

NMHC (ppmC): 1-10

$\text{NO}_x$  (20%  $\text{NO}_2$ ) (ppm) : 0.1-1.0

The ratio range is:

$\text{NMHC}/\text{NO}_x$  : 7-20

Figure 6 delineates all possible combinations with these concentrations and ratios.

Table 2. Dilution Rate (24-Hour Dilution)

Throughput in 24 Hours $\frac{F}{V} \times t$ in Percent V	Actual Flow Rate, $\text{m}^3 \text{ min}^{-1} \times 10^2$	Percent Original Volume Left After 24 Hours of Dilution at the Specified Flow Rate	Percent Dilution in 24 Hours
300	5.83	5.0	95
150	2.92	22.3	77
50	0.96	60.7	39
0	Sample Replacement	96.0	4

Table 3. Selected Experimental Conditions,  
Contract (68-02-1296)

NMHC/NO <sub>x</sub> Ratios: 95% Dilution in 24 Hours Starting at:		77% Dilution in 24 Hours Starting at:	
Sunrise		NO <sub>x</sub> Crossover	
10/1		10/1	
5/.71		5/.71	
5/.24		5/.24	
1/.1		1/.1	
NO <sub>x</sub> Crossover		NO <sub>x</sub> Crossover	
10/1		10/.75	
5/.71		5/.50	
5/.24		5/.36	
1/.1		1/.14	
1700		No Dilution (Batch)	
10/1		10/1	
5/.71		5/.71	
5/.24		5/.24	
1/.1		1/.1	

Table 4. Experimental Conditions,  
Extended Project\*

Time of Initiation of Dilution	% Dilution in 24 Hours	Reagent Concentrations HC/NO <sub>x</sub>	Number of Runs
None (Batch)	0	10/1, 1/.1, 5/.71, 5/.24	4
Sunrise	39	10/1, 1/.1, 5/.71, 5/.24	4
	95	10/1, 1/.1, 5/.71, 5/.24	4
1700 EDT - RTP, N.C.	39	10/1, 1/.1, 5/.71, 5/.24	4
	95	10/1, 1/.1, 5/.71, 5/.24	4
NO <sub>x</sub> Crossover	39	10/1, 1/.1, 5/.71, 5/.24	4
	77	10/1, 1/.1, 5/.71, 5/.24 10/.48, 10/.75, 5/.36, 5/.50, 1/.14	9
	95	10/1, 1/.1, 5/.71, 5/.24	4

Total Number, Sets of Conditions 37

Replications 7

Total Runs 44

\* See Table 3 for Runs on Contract (68-02-1296).

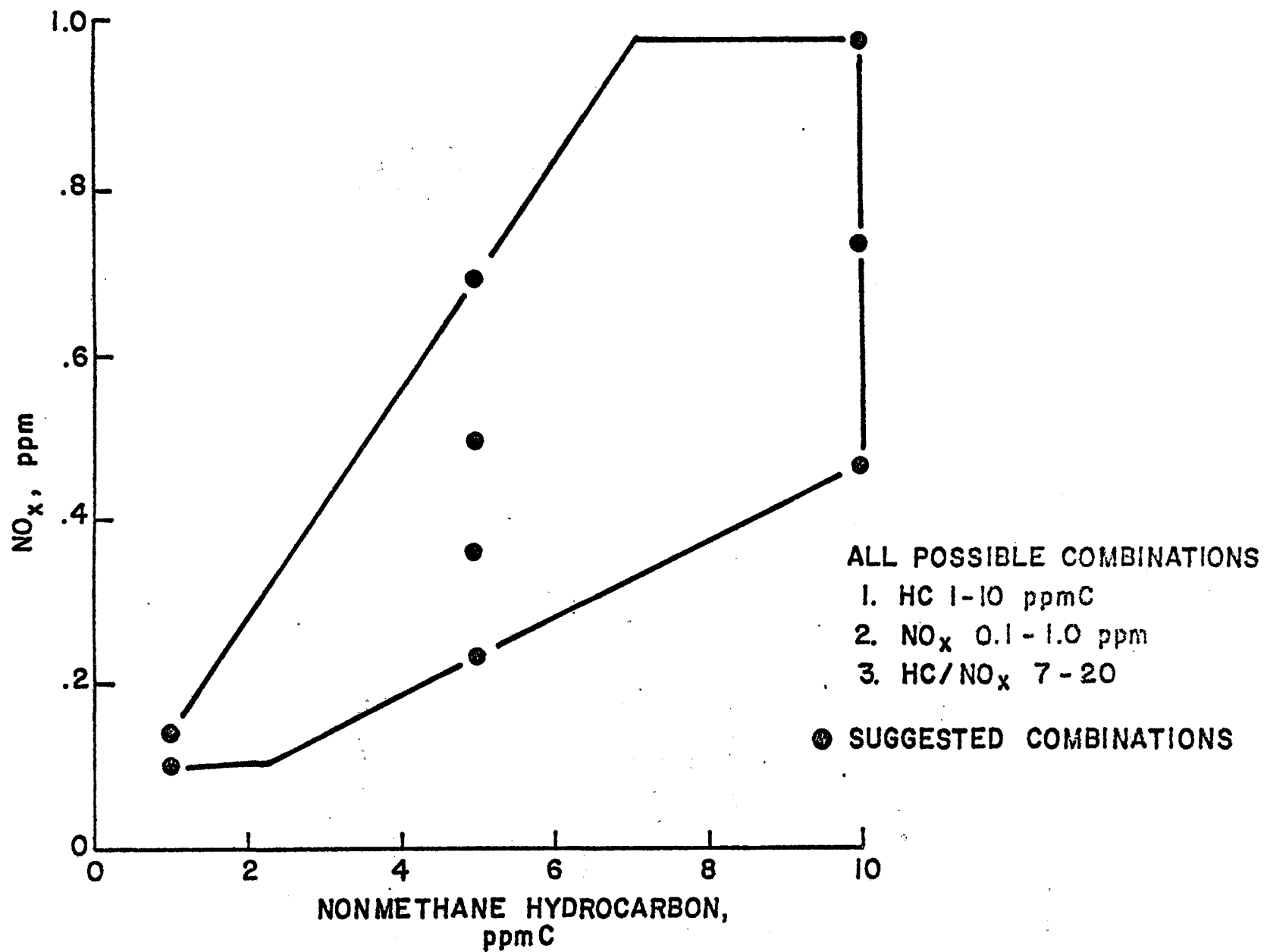


Figure 6. Range of all possible combinations of NO<sub>x</sub> and nonmethane hydrocarbon concentrations used in experimental work.

The purpose of the study was to study the  $O_3$ -precursor relationship under conditions of simulated meteorological transport. Two facets of transport were employed, urban pollution mixtures were exposed to outdoor conditions for 60 hours beginning at sunrise the first day, and the urban pollution system was diluted with clean air. The dilution was initiated at different times of the day and continued at different rates for 24 hours, after which the system was run on a batch basis. Dilution was terminated after 24 hours because it is probable that in the eastern United States air with which the system is being mixed is just as polluted as the urban system it is diluting.

## REAGENTS

The HC mixture used was constituted so as to represent a reasonable surrogate of Los Angeles air. The following fractions and ratios were determined on a carbon basis. The alkane/alkene/acetylene/aromatic percentages were 49/22/9/20. Propane, n-butane, isopentane and cyclopentane constituted the alkane fraction in ratios of 1.0/3.4/2.1/0.06. Propane represented itself; n-butane, the straight chain alkanes; isopentane, the branched chain alkanes; and cyclopentane, the cyclic paraffins. Ethylene, propylene, butene-1, trans-2-butene and 2-methyl-butene-2 constituted the alkene fraction in ratios of 1.0/0.32/0.39/0.21/0.29. Ethylene and propylene represented themselves, butene-1 represented terminally double-bonded compounds, butene-2 represented internally double-bonded compounds, and 2-methyl-butene-2 represented branched-chain olefins. The aromatic compounds were represented by toluene. In all cases, the  $NO_x$  injected was 20%  $NO_2$  and 80%  $NO$ .

## MEASUREMENT METHODS

### Continual Instrumental Measurements

Ozone, NO, NO<sub>2</sub>, total hydrocarbons (THC), methane (CH<sub>4</sub>), and CO were measured on a continual basis by use of automated instruments described below. Calibration was performed prior to each three-day experiment.

Ozone was detected by use of the chemiluminescent reaction between O<sub>3</sub> and ethylene. The Bendix instrument was used. A stable ultraviolet light O<sub>3</sub> generator of known output serves as the calibration source. The output of the O<sub>3</sub> generator itself was determined by the neutral-buffered KI procedure for O<sub>3</sub> and/or by gas-phase titration of a certified standard of NO in nitrogen mixture.

Nitric oxide and NO<sub>2</sub> were both detected by use of the chemiluminescent reaction between NO and O<sub>3</sub>. In this instrument the NO<sub>2</sub> is catalytically converted to NO. A Bendix instrument and a TECO Model 14 were employed. Calibration of the NO and NO<sub>x</sub> channels of the instrument was performed by dilution of a certified cylinder of NO in N<sub>2</sub>. The NO<sub>2</sub> channel was calibrated with NO<sub>2</sub> produced from the gas-phase titration of known NO concentrations with O<sub>3</sub> from the calibrated ozone generator.

Total hydrocarbons, CH<sub>4</sub>, and CO were determined by an automatic environmental chromatograph equipped with a flame ionization detector. The Beckman Model 6800 was employed. Calibration was performed by introduction of a certified mixture of CH<sub>4</sub> and CO. This instrument was calibrated at 12-hour intervals during each three-day experiment.

### Periodic Measurements: Hydrocarbons, Oxidant, Nitrogen Dioxide, Formaldehyde, and Condensation Nuclei

Individual hydrocarbons and selected products of photochemical reaction were determined by gas chromatographic separation and flame ionization detection from samples taken twice daily. A modified Perkin-Elmer Model 900 chromatograph was used.

Air samples taken from ports at the individual reaction chambers were passed through a metal bellows pump into a Tedlar bag. A permanganate in-line scrubber destroyed the O<sub>3</sub> and thus stabilized the HC composition of the sample.

A specific volume of sample from the Tedlar bag was trapped in a 0.0032-m ID stainless steel loop which had been immersed in liquid oxygen. The trap was connected to the chromatograph, heated, and its contents passed into the column.

Low-molecular-weight hydrocarbons ( $C_2-C_5$ ) were separated by a 1.8-m  $\times$  0.0032-m SS column packed with n-octane on Porasil. The column was at 23°C with a carrier flow rate of 12 ml per minute.

High-molecular-weight hydrocarbons (including aromatics) were separated by a 1.8-m  $\times$  0.0032-m SS column packed with GP 5% SI-1200/5% Bentone 34 on 100/120 Supelcoport. The column was at 75°C with a carrier flow rate of 20 ml per minute.

The chromatograph detector response and retention times were reestablished on at least every second working day by introduction of known hydrocarbons from certified cylinders of  $\pm 1\%$  accuracy. A Hewlett-Packard Model HP-3352 gas chromatographic data system acquired peak area data and printed out the results on a teletype.

Ozone,  $NO_2$ , and formaldehyde ( $CH_2O$ ) were determined by wet chemistry techniques employing impingers and spectrophotometric detection. The neutral-buffered potassium iodide procedure was used for  $O_3$  determination, and the Saltzman procedure was used for  $NO_2$  determination (ref. 2). Formaldehyde was collected and detected using the chromotropic acid procedure, Inter-society Committee, Procedure No. 110 (ref. 3). Calibration curves and blanks were prepared periodically according to the procedures referenced above. The determinations were performed twice daily, at 0900 and 1600 EDT.

A measure of condensation nuclei (CN) was determined four times per day. A Gardner Associates Type CN detector was used. The sample was taken directly from the chamber through a 1-m length of Teflon tubing. The manufacturer's calibration was used.

#### Radiation

Total solar radiation (TSR) was followed with a Kipp and Zonen solarimeter. This instrument was used as a guide to the radiation behavior for the day's experiment. The TSR and UV radiometer data collected by the EPA Division of Meteorology at a point approximately 500 m distant from the RTI smog chamber site were used for quantitative purposes.

## SECTION VI

### DISCUSSION OF RESULTS

The results of this study can be used to explain many of the major features of the high nonurban  $O_3$  concentrations observed in the eastern United States in recent years. This air is generally characterized by concentrations of several tens of parts per million of NMHC (e.g., 0.50 ppm), a few tens of parts per billion (e.g., 0.015 ppm) of  $NO_x$  and generally 0.08 to 0.20 ppm of  $O_3$ . (Data from gas chromatographic analyses of individual hydrocarbons are presented in Appendix A. Ozone,  $NO_x$ , NMHC, CO, and solar radiation data are presented as computer-printed graphs in Appendix B. Because the individual data are too voluminous for inclusion in this report, they have been supplied separately to EPA on computer cards and as computer-generated listings.)

It is postulated that the chemistry of the generation of high  $O_3$  concentrations downwind from a city involves the following three major processes:

1. Once generated in a "spent photochemical" system (i.e., low  $NO_x$ , virtually no alkenes) and, out of touch with new sources of precursors,  $O_3$  is not destroyed rapidly and can persist overnight in high concentrations.

The half-life of  $O_3$  in the field, held aloft, away from pollution sources was estimated from one set of vertical  $O_3$  soundings to be 20 to 30 hours. This is not unreasonable for  $O_3$  in a mature photochemical system out of touch with  $O_3$ -destructive agents which may be present in recently polluted air parcels. The half-lives of  $O_3$  in the chamber runs generally were between 3 and 10 hours.

2. For systems of comparable hydrocarbon/ $NO_x$  ratio, dilution of the system, whether reduction of the initial concentrations or dynamic dilution after the initiation of irradiation, leads to the generation of more  $O_3$  per precursor molecule.
3. The third process included in the generation of nonurban  $O_3$  in high concentrations involves the  $NO$ - $NO_2$ - $O_3$  cycle. As a photochemical system reacts, the olefins disappear more rapidly than the aromatics and the alkanes. The  $NO_x$  concentration is reduced even more rapidly



than the NMHC. It is postulated that as the NMHC/NO<sub>x</sub> ratio increases, the hydroxyl radicals generated in the system react in larger and larger proportions with the hydrocarbons than with NO<sub>2</sub>. Reactions of an hydroxyl with an organic molecule leads eventually to the oxidation of NO to NO<sub>2</sub>, thus preserving one O<sub>3</sub> molecule. Reaction of the hydroxyl with NO<sub>2</sub> leads to the formation of HONO<sub>2</sub>. This reaction removes an NO<sub>x</sub> molecule from the system and does not lead to the generation of an O<sub>3</sub> molecule. When the NO<sub>x</sub> molecules are diluted sufficiently, the absolute rate of generation of O<sub>3</sub> is so low that it cannot replace O<sub>3</sub> lost by various extraneous reactions always taking place in the system. In reaction and dilution, depending on original conditions, the net O<sub>3</sub> generated per NO<sub>x</sub> cycle increases more rapidly than the total decrease in O<sub>3</sub> by dilution, destruction, and synthesis inhibition--up to a point. At some level the NO<sub>x</sub> molecules become so few that they cannot supply a net increase in O<sub>3</sub> in the face of the various destructive processes such as photochemically related destruction of O<sub>3</sub>, heterogeneous destruction, and reaction with substances generally not considered as part of the photochemical oxidant systems.

Data from this study support the hypothesis that these processes are active in the generation of high rural O<sub>3</sub> concentrations.

## OZONE-PRECURSOR RELATIONSHIPS

The data were examined to determine the effect of concentration and ratio of the measured oxidant precursors at the beginning of solar irradiation on subsequent  $O_3$  maxima and on net  $O_3$  generated. The pertinent data are summarized in Tables 5, 6, 7, 8, 9, and 10.

The relationship among initial concentrations of  $NO_x$  and NMHC concentration and subsequent  $O_3$  maximum concentration on second and third days of irradiation as revealed in this study is, as expected, quite different from that of the more classical smog chamber studies (ref. 1). Tables 11, 12, 13, and 14 illustrate this point. The ranges of concentrations and NMHC/ $NO_x$  ratios used in making the tables were chosen arbitrarily in an attempt to place a number of cases in each category. These data are plotted in Figures 7, 8, and 9.

Hydrocarbon mixtures on the second and third day of irradiation were, as expected, much lower in olefins than was the initial mixture. On the second and third day of solar irradiation the butene was seldom as high as 2 ppbC, propylene was at or (usually) below 2 ppbC (except in the batch runs when it was 2, 5, 12, and 15 ppbC on the second day) and ethylene was generally in the low 10's of ppbC. The mix contained essentially alkanes and aromatics by the second day. (Hydrocarbon analyses are presented in Appendix A.)

The greater the  $NO_x$  concentration at sunrise on the second and third days the greater the subsequent net  $O_3$  ( $\Delta O_3$ ) generated; for example, the 1-5 ppb  $NO_x$  concentrations produced an average  $\Delta O_3$  of 0.149 ppb; 6-8 ppb  $NO_x$ , a  $\Delta O_3$  of 0.171 ppm; 9-14 ppb  $NO_x$ , 0.180 ppm  $\Delta O_3$ ; and 15-53 ppb  $NO_x$ , 0.241  $\Delta O_3$ . For the same ranges of  $NO_x$  the subsequent maximum  $O_3$  concentrations were 0.180 ppm, 0.254 ppm, 0.259 ppm, and 0.454 ppm. This also shows that average daily minimum increased with increasing  $NO_x$  range: 0.031, 0.083, 0.079, and 0.213 ppm (see Figure 7).

Average  $\Delta O_3$  values corresponding to NMHC concentration ranges for: 0-0.49 ppmC was 0.157 ppm; 0.50-0.99 was 0.180; 1.00 to 1.99, was 0.183; and  $\geq 2.00$ , was 0.257. The corresponding maximum  $O_3$  concentrations were 0.175, 0.241, 0.301, and 0.623 ppm.

Table 5. Selected Results From the July 17-18 Two-Day Chamber Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO <sub>x</sub> Concentrations ppmC/ppm	NMHC/NO <sub>x</sub> Ratios	Maximum O <sub>3</sub> First Day ppm	Subsequent Days	Precursors (ppm) at Sunrise		NMHC/NO <sub>x</sub> Ratios <sup>x</sup>	Min O <sub>3</sub> ppm	Max O <sub>3</sub> ppm	Net O <sub>3</sub> ppm	Σ Solar Rad. at O <sub>3</sub> Max (Langley's)
						NO <sub>x</sub>	NMHC					
Chamber No. 1 July 17-18	95% @ Sunrise	<u>6.68</u> 0.410	16.2	0.310	2	0.014	0.470	33.6	.005	.200	.195	407.4 <sup>n</sup>
	0610 Start				3							
Chamber No. 2 July 17-18	0610	<u>3.71</u> 0.125	29.7	0.385	2	0.015	0.330	22.0	.000	.181		407.4
					3							
Chamber No. 3 July 17-18	0610	<u>3.49</u> 0.293	11.9	0.141	2	0.015	0.360	24.0	.001	.155	.154	410.4
					3							
Chamber No. 4 July 17-18	0610	<u>1.19</u> 0.046	25.9	0.182	2	0.013	0.330	25.4	.001	.116	.115	406.8
					3							

Table 6. Selected Results From the July 22-24 Three-Day Chamber Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO <sub>x</sub> Concentrations ppmC/ppm	NMHC/NO <sub>x</sub> Ratios	Maximum O <sub>3</sub> First Day ppm	Subsequent Days	Precursors (ppm) at Sunrise		NMHC/NO <sub>x</sub> Ratios <sup>x</sup>	Min O <sub>3</sub> ppm	Max O <sub>3</sub> ppm	Net O <sub>3</sub> ppm	Σ Solar Rad. at O <sub>3</sub> Max (Langley's)
						NO <sub>x</sub>	NMHC					
Chamber No. 1 July 22-24	95% @ 1700	<u>11.45</u> .958	12.0	1.57	2	0.015	1.78	118.7	.035	.185	.150	427.8
					3	0.010	1.07	107.0	.016	.323	.307	480.6
Chamber No. 2 July 22-24	1700	<u>4.47</u> .231	19.4	0.950	2	0.009	1.30	144.4	.015	.138	.123	490.2
					3	0.007	0.94	134.3	.010	.260	.250	480.6
Chamber No. 3 July 22-24	1700	<u>4.11</u> .685	6.0	1.196	2	0.010	1.18	118.0	.025	.119	.094	487.8
					3	0.007	0.89	127.1	.011	.268	.257	488.4
Chamber No. 4 July 22-24	1700	<u>1.76</u> .103	17.1	0.625	2	0.004	0.95	237.5	.013	.089	.076	487.8
					3	0.005	0.72	144.0	.008	.225	.217	488.4

Table 7. Selected Results from the July 28-30 Three-Day Chamber Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO <sub>x</sub> Concentrations ppmC/ppm	NMHC/NO <sub>x</sub> Ratios	Maximum O <sub>3</sub> First Day ppm	Subsequent Days	Precursors (ppm) at Sunrise		NMHC/NO <sub>x</sub> Ratios	Min O <sub>3</sub> ppm	Max O <sub>3</sub> ppm	Net O <sub>3</sub> ppm	Σ Solar Rad. at O <sub>3</sub> Max (Langley's)
						NO <sub>x</sub>	NMHC					
Chamber No. 1  July 28-30	95% @  0830	<u>7.02</u> .967	7.3	1.062	2	0.007	0.84	120.0	.023	.286	.263	515.4
					3	0.009	0.85	94.4	.050	.240	.190	421.2
Chamber No. 2  July 28-30	0840	<u>4.24</u> .235	18.0	0.604	2	0.003	0.77	256.7	.006	.212	.206	535.2
					3	0.005	0.76	152.0	.038	.190	.152	420.6
Chamber No. 3  July 28-30	0840	<u>3.95</u> .715	5.5	0.667	2	0.005	0.48	96.0	.013	.214	.201	534.6
					3	0.005	0.55	110.0	.037	.190	.153	397.8
Chamber No. 4  July 28-30	0850	<u>1.15</u> .105	11.0	0.325	2	0.002	0.55	275.0	.003	.175	.172	541.2
					3	0.003	0.63	210.0	.042	.167	.125	427.2

Table 8. Selected Results From the August 4-6 Three-Day Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO <sub>x</sub> Concentrations ppmC/ppm	NMHC/NO <sub>x</sub> Ratios	Maximum O <sub>3</sub> First Day ppm	Subsequent Days	Precursors (ppm) at Sunrise		NMHC/NO <sub>x</sub> Ratios <sup>x</sup>	Min O <sub>3</sub> ppm	Max O <sub>3</sub> ppm	Net O <sub>3</sub> ppm	Σ Solar Rad. at O <sub>3</sub> Max (Langley's)
						NO <sub>x</sub>	NMHC					
Chamber No. 1 August 4-6	77% @ 0810	$\frac{7.35}{.936}$	7.9	1.338	2	0.017	1.13	66.5	.114	.479	.365	554.7
					3	0.012	0.79	65.8	.174	.293	.119	318.4
Chamber No. 2 August 4-6	0820	$\frac{4.41}{0.232}$	19.0	0.806	2	0.009	0.88	97.8	.054	.366	.312	511.2
					3	0.006	0.62	103.3	.128	.233	.105	318.4
Chamber No. 3 August 4-6	0830	$\frac{4.40}{.675}$	6.5	0.956	2	0.010	0.74	74.0	.094	.350	.256	511.2
					3	0.007	0.58	82.9	.114	.238	.124	291.7
Chamber No. 4 August 4-6	0805	$\frac{1.09}{.107}$	10.2	0.488	2	0.001	0.61	610.0	.041	.214	.173	554.7
					3	0.004	0.47	117.5	.056	.179	.123	318.4

Table 9. Selected Results From the August 8-10 Three-Day Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO <sub>x</sub> Concentrations ppmC/ppm	NMHC/NO <sub>x</sub> Ratios	Maximum O <sub>3</sub> First Day ppm	Subsequent Days	Precursors (ppm) at Sunrise		NMHC/NO <sub>x</sub> Ratios	Min O <sub>3</sub> ppm	Max O <sub>3</sub> ppm	Net O <sub>3</sub> ppm	Σ Solar Rad. at O <sub>3</sub> Max (Langley's)
						NO <sub>x</sub>	NMHC					
Chamber No. 1  August 8-10	77% @ 0940	<u>5.81</u> 0.717	8.1	0.991	2	0.020	1.01	50.5	.100	.400	.300	513.0
					3	0.014	0.52	37.1	.136	.318	.182	309.6
Chamber No. 2  August 8-10	0850	<u>3.52</u> 0.347	10.1	0.841	2	0.010	0.64	64.0	.063	.293	.230	570.0
					3	0.008	0.62	78.0	.109	.231	.122	309.6
Chamber No. 3  August 8-10	0940	<u>3.09</u> 0.481	6.4	0.688	2	0.012	0.62	51.7	.074	.288	.214	564.0
					3	0.010	0.84	84.0	.100	.248	.148	266.4
Chamber No. 4  August 8-10	0940	<u>0.93</u> 0.144	6.5	0.378	2	0.002	0.43	215.0	.050	.179	.129	570.0
					3	0.004	0.71	178.0	.071	.163	.092	304.8

Table 10. Selected Results From the August 12-14 Three-Day Runs

Date Chamber No.	Percent Dilution, Time of Dilution Initiation	Initial NMHC/NO <sub>x</sub> Concentrations ppmC/ppm	NMHC/NO <sub>x</sub> Ratios	Maximum O <sub>3</sub> First Day ppm	Subsequent Days	Precursors (ppm) at Sunrise		NMHC/NO <sub>x</sub> Ratios <sup>x</sup>	Min O <sub>3</sub> ppm	Max O <sub>3</sub> ppm	Net O <sub>3</sub> ppm	Σ Solar Rad. at O <sub>3</sub> Max (Langley's)
						NO <sub>x</sub>	NMHC					
Chamber No. 1 August 12-14	Static	$\frac{7.73}{0.938}$	8.2	1.37	2	0.053	3.78	71.3	.527	.724	.197	595.2
					3	0.033	3.01	91.2	.270	.614	.344	547.8
Chamber No. 2 August 12-14		$\frac{4.34}{0.225}$	19.5	0.886	2	0.022	2.62	119.1	.390	.525	.135	595.2
					3	0.018	2.10	116.7	.228	.466	.238	548.4
Chamber No. 3 August 12-14		$\frac{3.81}{0.676}$	5.6	0.997	2	0.039	2.49	63.8	.415	.609	.194	600.6
					3	0.019	1.93	101.6	.246	.474	.228	548.4
Chamber No. 4 August 12-14		$\frac{1.56}{0.103}$	15.2	0.549	2	0.011	1.30	118.2	.303	.336	.033	591.6
					3	0.007	1.13	161.4	.191	.259	.068	594.6



Table 11. Net Ozone Generated on Second and Third Days of Irradiation  
as a Function of Oxides of Nitrogen and Nonmethane Hydro-  
carbon/Oxides of Nitrogen Ratio

NMHC NO <sub>x</sub> ppmC Range ppm	NO <sub>x</sub> Range ppb	1 - 5	6 - 8	9 - 14	15 - 53
0-49				.195 .115 *.182	.164 avg. .181 .154 .168 avg.
.165					
50-99	.201   				

\*Indicates 3rd-Day Values.

Table 12. Maximum Ozone Concentration on Second and Third Days of Irradiation  
as a Function of Oxides of Nitrogen and Nonmethane Hydrocarbon/  
Oxides of Nitrogen Ratio

$\frac{\text{NMHC}}{\text{NO}_x}$ ppmC Range ppm	$\text{NO}_x$ Range ppb	1 - 5	6 - 8	9 - 14	15 - 53
0-49				.200 .116 *.318	.211 avg. .181 .155 .168 avg.
.194					
50-99	.214	.214 avg.	*.238 *.231 .235 avg.	.366 .350 .293 .288 *.240 *.293 *.248	.297 avg. .479 .400 .724 .786 *.614 .601 avg.
.384					
100-199	*.190 *.225 *.190 *.179 *.163	.189 avg.	.286 *.260 *.268 *.233 *.259	.261 avg. .138 .119 .336 *.322	.229 avg. .185 .525 *.466 *.474 .413 avg.
.268					
>200	.089 .212 .175 .214 .179 *.167	.173 avg.			
Avg. .173		Avg. .180	Avg. .254	Avg. .259	Avg. .454

\* Indicates 3rd-Day values.

Table 13. Net Ozone Generated on Second and Third Days of Irradiation  
as a Function of Nonmethane Hydrocarbon and Nonmethane  
Hydrocarbon/Oxides of Nitrogen Ratio

$\frac{\text{NMHC}}{\text{NO}_x} \frac{\text{ppmC}}{\text{ppm}}$	NMHC Range ppmC								
Ratio	ppm		0 - .49		.50 - .99		1.00 - 1.99		$\geq 2.00$
0-49	.195 .181 .154 .115	<u>.161</u> avg.	*.182	<u>.182</u> avg.					
.165									
50-99	.201	<u>.201</u> avg.	.312 .256 .230 .214 *.190 *.119 *.124	*.131 *.177 <u>.195</u> avg.	.365 .300	<u>.333</u> avg.	.197 .371 *.344	<u>.304</u> avg.	
.235									
100-199	*.123	<u>.123</u> avg.	.263 *.250 *.257 *.217 *.152 *.153 *.105	*.054 <u>.181</u> avg.	.150 .123 .094 .033 *.285 *.228 *.068	<u>.140</u> avg.	.135 *.238	<u>.187</u> avg.	
.163									
>200	.129	<u>.129</u> avg.	.076 .206 .172 .173 *.125	<u>.150</u> avg.					
Avg. .147		Avg. .157		Avg. .180		Avg. .183		Avg. .257	

\* Indicates 3rd-Day Values.

Table 14. Maximum Ozone Concentration on Second and Third Days of Irradiation as a Function of Nonmethane Hydrocarbon and Nonmethane Hydrocarbon/Oxides of Nitrogen Ratio

$\frac{\text{NMHC}}{\text{NO}_x}$ ppmC Ratio ppm	NMHC Range ppmC	0 - .49	.50 - .99	1.00 - 1.99	$\geq 2.00$
0-49	.200 .181 .155 .116	<u>.163</u> avg.	*.318 <u>.318</u> avg.		
.194					
50-99	.214	<u>.214</u> avg.	.366 *.231 .350 *.248 .293 .288 *.240 *.293 *.238	.479 .400 <u>.440</u> avg.	.724 .786 *.614 <u>.708</u> avg.
.384					
100-199	*.179	<u>.179</u> avg.	.286 *.163 *.260 *.268 *.225 *.190 *.190 *.233	.185 .138 .119 .336 *.322 *.474 *.259	.525 *.466 <u>.496</u> avg.
>200	.179	<u>.179</u> avg.	.089 .212 .175 .214 *.167	<u>.171</u> avg.	
Avg. .173		Avg. .175	Avg. .241	Avg. .301	Avg. .623

\* Indicates 3rd-Day Values.

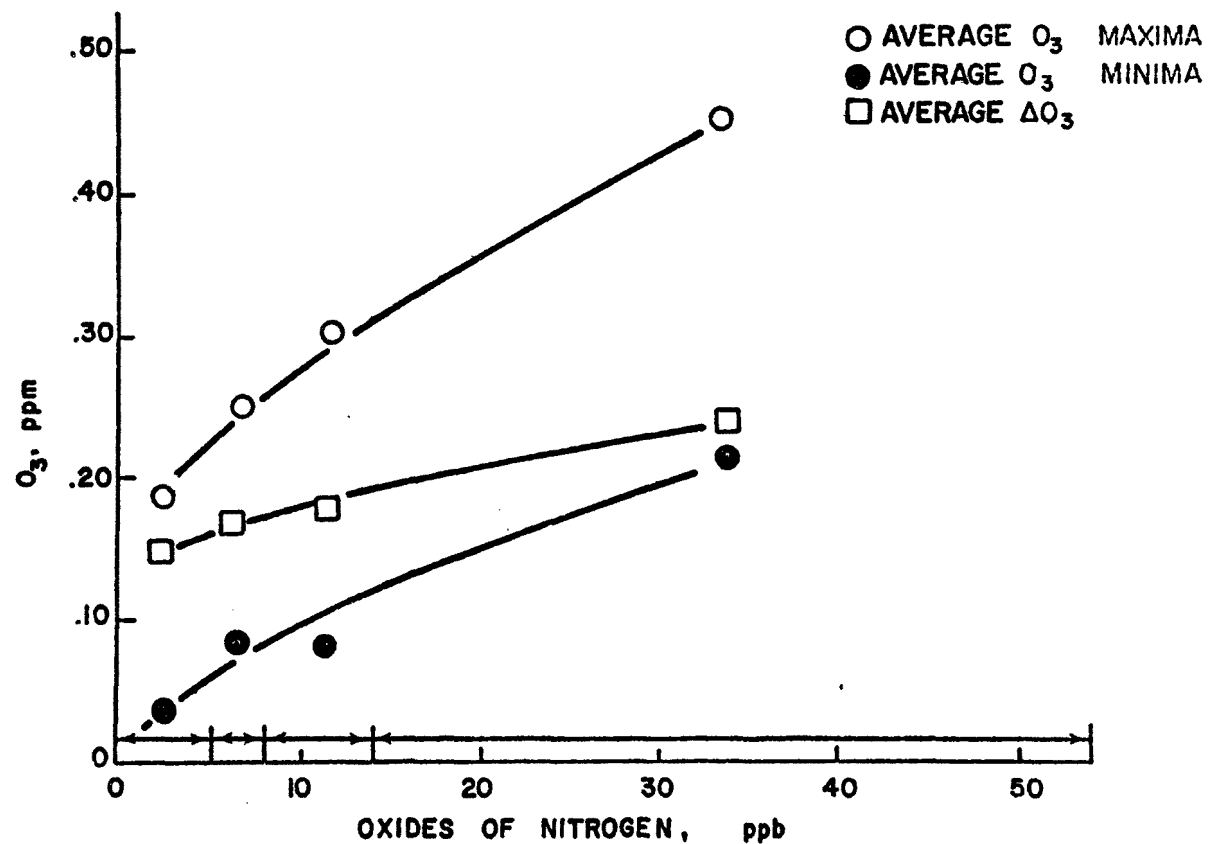


Figure 7. Average maxima, minima, and  $\Delta O_3$  concentrations as a function of  $NO_x$  concentrations at sunrise on the second and third days of irradiation.

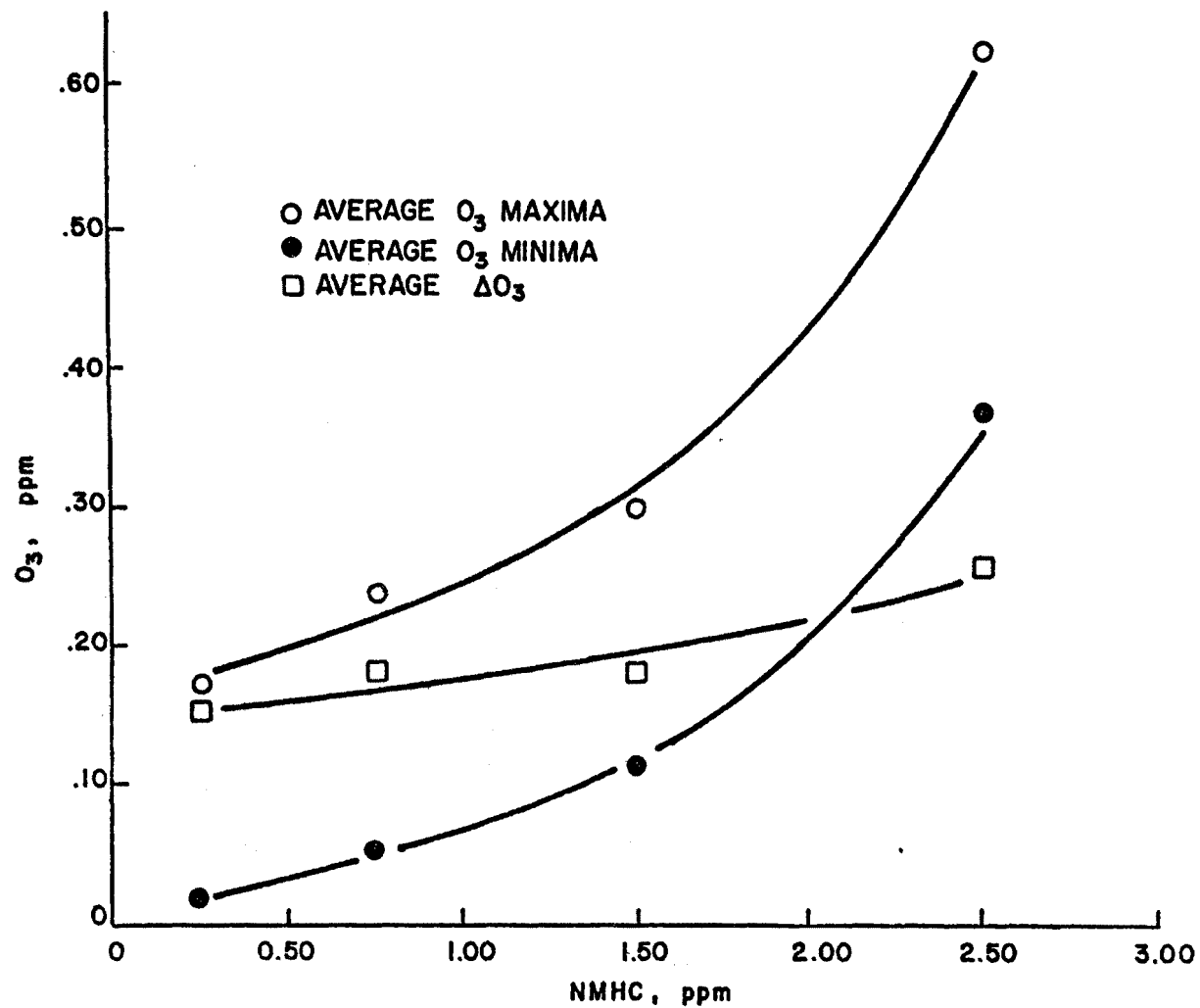


Figure 8. Average maxima, minima, and  $\Delta O_3$  concentrations as a function of nonmethane hydrocarbon concentrations on the second and third days of irradiation.

Increasing hydrocarbon concentration at sunrise of the second and third days tended also to increase the subsequent net  $O_3$  generation as can be seen in Figure 8.

For the NMHC/ $NO_x$  ratios, the  $\Delta O_3$  for the range 0-49 was 0.165; for 50-99 it was 0.235; for 100 to 199 it was 0.163; and for  $>200$  it was 0.147. Maximization of  $O_3$  concentration occurred in the 50-99 range (see Figure 9).

It can be demonstrated, in any case, that low concentrations of  $NO_x$  (i.e., 0-5 ppb, within the noise level of the chemiluminescent  $NO_x$  meters) will generate  $O_3$  in concentrations above the NAAQS. In almost all cases (the exceptions will be mentioned below) the second-day net  $O_3$  generated was greater than the third-day net  $O_3$ .

Although no PAN data have been obtained, the difference between  $NO_2$  determined by the Saltzman procedure and the chemiluminescent instrument indicates the presence of nitroxy compounds other than NO and  $NO_2$ .

In general, second-day maximum net  $O_3$  generation was greater than third-day net  $O_3$ , which was expected (Tables 6 and 10). In the static (no dilution) runs and in the runs diluted 95% in 24 hours (dilution initiated at 1700 of the first day), the reverse was the case, even though the cumulative sunlight to time of  $O_3$  maximum was comparable for the series of 2 days.

Although there is no readily apparent explanation of this anomaly in the data, it should be noted that at the time of maxima in the dilution runs on the second day, the system was still operating in the dilution mode. On the third day it was operating in the batch mode. On the second day, the combination of destruction plus mechanical removal of  $O_3$  must be balanced against synthesis whereas on the third day only chemical reaction was removing  $O_3$  as it was generated.

In the case of the static or batch runs, the explanation for a greater net  $O_3$  generation on the third day than the second has to be different, but again there is not an immediately apparent reason for the difference.

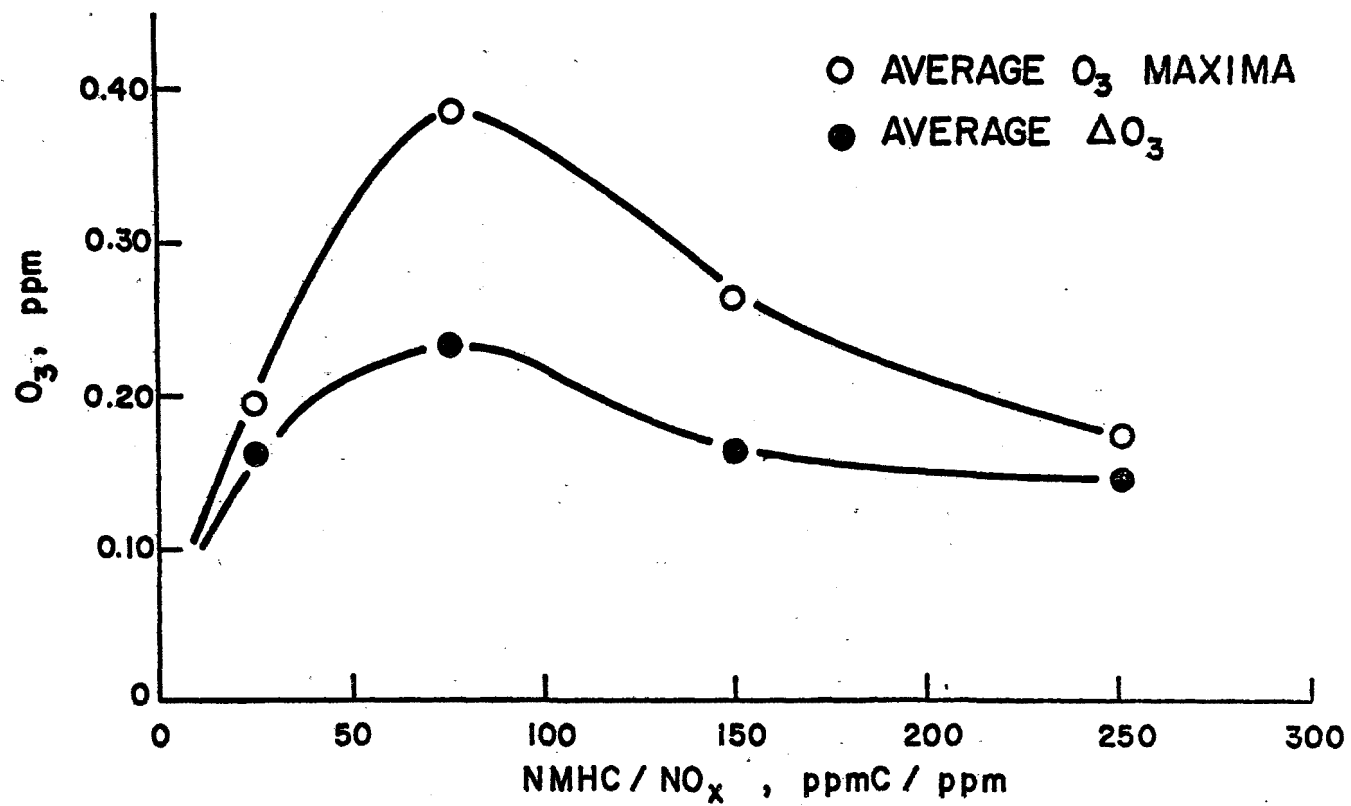


Figure 9. Average maxima and  $\Delta O_3$  as a function of nonmethane hydrocarbon to oxides of nitrogen ratio.



## "FOSSIL" OZONE

One of the processes which are operative in the occurrence of high concentrations of  $O_3$  in rural areas is the low rate of  $O_3$  destruction in photochemically "spent" pollution systems. ("Spent" means here that the system has been reacting photochemically, the  $NO_x$  concentrations are low [a few parts per billion], and the olefinic content of the air has been exhausted, or nearly so.) This  $O_3$  is often referred to as "fossil" ozone, perhaps an unfortunate adjective to apply, but the lifetime of "fossil"  $O_3$  is seldom, if ever, specified, even vaguely.

Ozone measured at or near the ground (e.g., at 1.0 m) has the opportunity to engage not only in gas-phase homogeneous reactions including photolysis, but also in heterogeneous reactions with the ground and other surfaces.

Under conditions of atmospheric subsidence, there is the possibility of considerable thermal layering of the air with a considerable reduction of mass transport across thermal boundaries. At night, for example, a radiation inversion can be formed in the lower part of the previous day's mixing layer. The air between the bottom of the subsidence inversion and the top of the radiation inversion is effectively cut off from pollution emissions at the ground and dilution from above. Ozone, trapped in the remnant of the mixing layer, has only "left-over" precursors to react with, so an estimation of its duration will indicate how important both the trapped ozone and the subsequent synthesis are in maintaining the observed nonurban levels of  $O_3$  concentrations.

Nighttime half-lives for ground level  $O_3$  calculated from the hourly averages from three of the field stations in the 1974 RTI field study were 8.0, 8.2, and 9.7 hours (assuming first order decay). Calculated roughly from the ground level  $O_3$  values at Wilmington, Ohio (Figure 10), the half-life was about 10 hours. Calculated for the 600-m level in the same figure, the half-life of  $O_3$  aloft, out of touch with ground-based sources of pollution, was roughly 20 hours. (These last 2 calculations were based on the assumption that the vertical profile of  $O_3$  concentrations would be the same at 0700 on August 2 as on August 1.) The  $O_3$  destruction aloft, above the radiation inversion layer, is likely to be more representative of "fossil"

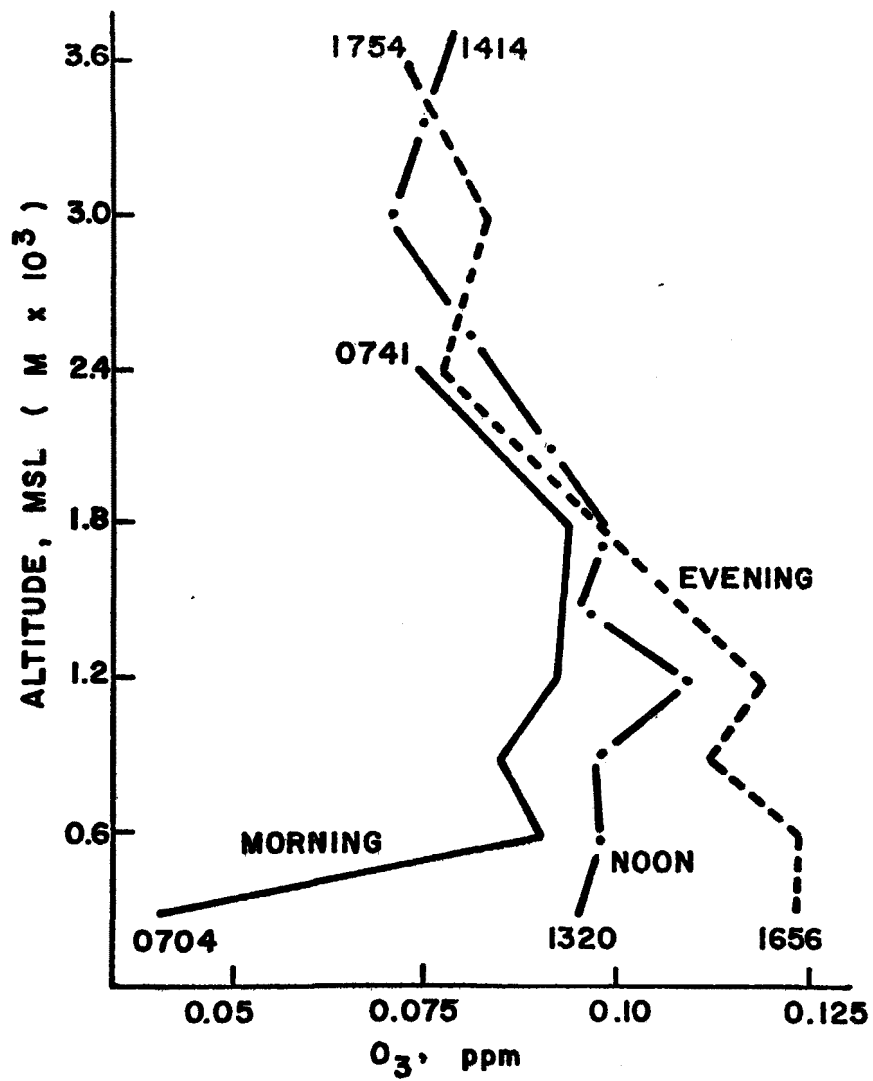


Figure 10. Vertical ozone soundings, August 1, 1974, Wilmington, Ohio.

O<sub>3</sub> conditions than O<sub>3</sub> destruction near the earth.

Dark-phase half-lives ( $t_{1/2}$ ) for O<sub>3</sub> in these chamber runs were calculated and are presented in Table 15. These half-lives were calculated from nighttime O<sub>3</sub> data taken at 0200 and 0500 when no dilution was occurring.

To get a feel for the dark gas-phase destruction of O<sub>3</sub>, consider the following table. Calculating O<sub>3</sub> destruction as a first order function with an assumed constant concentration of NO<sub>2</sub>, the concentration of NO<sub>2</sub> was calculated which would be required by the listed half-lives.

HALF-LIVES, Hours	CONSTANT CONCENTRATION OF NO <sub>2</sub> NECESSARY, ppm
1	.231
5	.046
10	.023
20	.012
30	.008
40	.006
50	.005

Calculations using most olefins would yield similar concentrations. Nitrogen dioxide can account for much of the O<sub>3</sub> disappearance at night in the chambers, but intermediates, such as aldehydes, may also contribute to dark phase O<sub>3</sub> decay both in chambers and in rural air.

In any event, a few hours half-life is sufficient to account for persistence of O<sub>3</sub> at detectable concentrations overnight. On the other hand, a half-life of 10 hours (it would be shortened in the sunlight) would reduce 0.200 ppm O<sub>3</sub> to .001 in 72 hours (3 days). This should offer an initial estimate of how far (or how long) "fossil" O<sub>3</sub> can be important without ongoing O<sub>3</sub> synthesis. Obviously the duration of significant concentrations of "fossil" O<sub>3</sub> depends on many factors, including the original urban concentration of O<sub>3</sub>. It is hardly likely that "fossil" O<sub>3</sub> alone, without concurrent daytime synthesis, can deliver O<sub>3</sub> concentrations in excess of the oxidant NAAQS to nonurban sites where transport processes have taken as long as 3 days. Therefore, persistence of O<sub>3</sub> in a "spent" photochemical

Table 15. Dark Phase Ozone Half-Lives in Smog Chamber Runs

Date	Experimental Type	Chamber Number	Max [O <sub>3</sub> ] Previous Day ppm	[O <sub>3</sub> ] at 0200 ppm	Half-Life ( $t_{1/2}$ ) hrs
July 24	Dilution 95% * Initiated at 1700	1	0.185	0.066	4.3
		2	0.138	0.048	3.6
		3	0.119	0.038	11.6
		4	0.089	0.025	13.3
July 30	Dilution 95% Initiated at NO <sub>x</sub> Crossover	1	0.286	0.102	6.4
		2	0.212	0.085	6.2
		3	0.214	0.076	7.4
		4	0.175	0.083	7.8
August 6	Dilution 77% Initiated at NO <sub>x</sub> Crossover	1	0.479	0.311	14.9
		2	0.366	0.243	11.6
		3	0.350	0.213	10.0
		4	0.214	0.109	7.1
August 10	Dilution 77% Initiated at NO <sub>x</sub> Crossover	1	0.400	0.218	16.6
		2	0.293	0.175	14.2
		3	0.288	0.150	19.2
		4	0.179	0.109	14.2
August 13	Batch	1	1.378	0.776	33.5
		2	0.886	0.561	42.9
		3	0.997	0.567	50.3
		4	0.549	0.415	265.4
August 14	Batch	1	0.724	0.422	19.9
		2	0.525	0.333	27.2
		3	0.786	0.352	54.5
		4	0.336	0.252	449.6

\* Mechanical dilution had been terminated prior to the time periods chosen for half-life calculations.

system appears to be important in the appearance of high nonurban concentrations of  $O_3$ , but usually must be supplemented by additional synthesis.

To calculate half-life:

$$\ln \frac{C_o}{C} = k_t t = [k_s + k_g] t$$

$C_o$  =  $O_3$  concentration at 0200

$C$  =  $O_3$  concentration at 0500

$t$  = 0500 - 0200 = 3 hours

$k_t$  = total rate =  $k_s + k_g$

$k_s$  = dark-phase rate constant from measured  $O_3$  decay in clean chamber air (system blank)

$k_g$  = rate constant in aged photochemical system

Solve for  $k_t$ ; and subtract  $k_s$  from  $k_t$  to obtain  $k_g$ .

$$t_{1/2} = \frac{\ln 2}{k_g}$$

## DILUTION EFFECT

Decrease of concentrations of precursors (at the same NMHC/NO<sub>x</sub> ratios) both by dynamic dilution and by decreasing initial concentrations in static systems resulted in an increase in the efficiency of O<sub>3</sub> generation per unit amount of precursors. In no case, when the initial precursors were at the same NMHC/NO<sub>x</sub> ratio and were diluted, was the resultant net O<sub>3</sub> concentration decreased by a similar percentage. In the batch runs, the decrease of O<sub>3</sub> concentrations was 59% for a 95% reduction of the initial concentration (10/1.0 to 1.0/0.1, hydrocarbon to NO<sub>x</sub>).

The effect of dynamic dilution is shown in Figure 11, which shows the second-day O<sub>3</sub> concentrations for 3 dilutions. The highest O<sub>3</sub> was obtained by the batch system (0.72 ppm) with ~100% of the original system left, the second highest O<sub>3</sub> was obtained in a 77% dilution system (0.40 ppm), and the lowest O<sub>3</sub> at 95% dilution (0.29 ppm). Dilution was initiated at the time of NO<sub>x</sub> crossover in both dilution systems. With 23% of the original system left, 75% as much O<sub>3</sub> was found as compared to the undiluted system and with 5% of the original system left, 40% as much O<sub>3</sub> was found.

If one compares the net O<sub>3</sub> increase ( $\Delta O_3$ ) (above minimum) for the second day, the chamber with 100% of the original system left had a  $\Delta O_3$  of 0.20 ppm while the system with 5% of the original system left had a  $\Delta O_3$  of 0.26 ppm. Total solar radiation was greater in the case of the static run. The net generation of O<sub>3</sub> was greater in the diluted case.

The time of initiation of dilution appears to influence second- and third-day ozone generation, but the data were too few to allow full delineation of the processes at work. The most notable effect of the time of initiation appears in the runs in which dilution was initiated at 1700. In these runs the net O<sub>3</sub> generated on the third day was approximately 2 to 3 times (1.9 to 2.9) as great as on the second day. The explanation may be that on the second day, mechanical dilution was decreasing the O<sub>3</sub> concentration at a rate which suppressed accumulation, enough to account for the low net generation, relative to the third day.

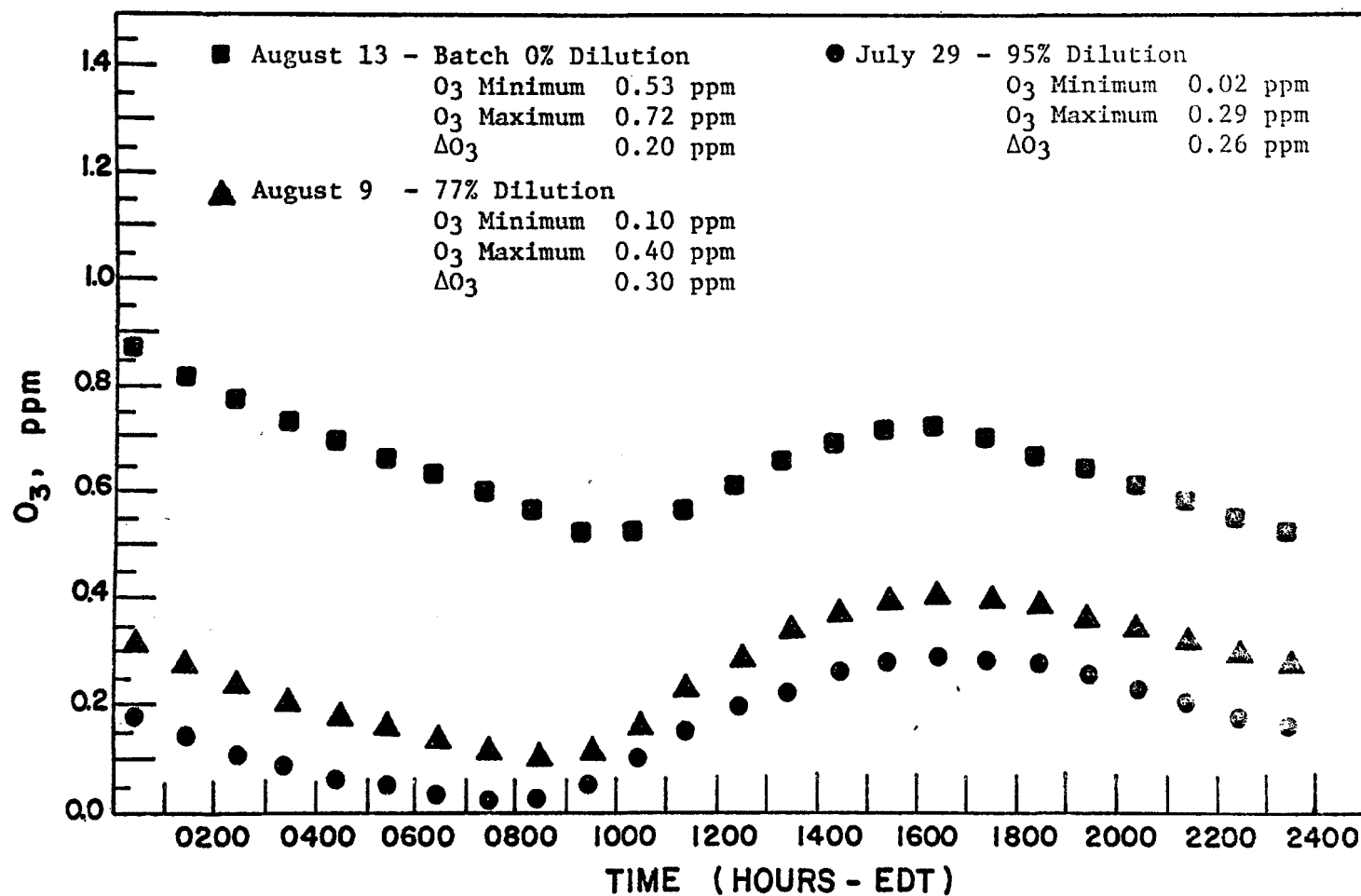


Figure 11. Ozone profiles over second-day irradiations for same initial conditions and different dilutions in Chamber #1.

These data indicate that dilution of an  $O_3$ -producing photochemical system does not reduce the maximum or the net  $O_3$  concentration in direct proportion to the extent of dilution. This increased efficiency of  $O_3$  production under dilution conditions is also supported by other findings (ref. 4). The dilution effect, therefore, is expected to be a significant contributor to the occurrence of high  $O_3$  concentrations at nonurban sites.



## COMPARISON OF FIELD OBSERVATIONS WITH SMOG CHAMBER RESULTS

The following comparisons of smog chamber results with field observations will be made with data from a study conducted in the summer of 1974 (ref. 5) unless otherwise noted. The results of the field study were reported in Report EPA-450/3-75-036 entitled Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies.

The hourly averages of  $O_3$  concentration for three rural sites are presented Figure 12. Hourly averages for  $NO_2$  at the rural stations are presented in Figure 13 and hourly averages for NMHC are given in Figure 14.

In the field study, the NAAQS for photochemical oxidant was exceeded approximately twice as frequently at nonurban as at urban stations. In 1974, frequently the urban maxima were lower than the rural maxima, although in a few cases, the reverse was true.

All smog chamber data are presented in the various appendixes, and  $O_3$  data from one run are presented in Figure 15 for easy comparison with the field data.

The experimental conditions for the first day of each chamber run were designed to represent the urban atmosphere, and the second and third days were to represent transported, "aged" photochemical systems. In all cases studied, the  $O_3$  generated on the first day was greater than that generated on subsequent days.

The analogy between chemical behavior on the first day of a smog chamber run and that observed in urban atmospheres is not good. The city  $O_3$  maxima are low compared with the first-day chamber maxima. Although the city data were, on the average, slightly lower than the rural data, they were generally comparable in value. Second- and third-day chamber data were always lower than the first-day smog chamber  $O_3$  concentrations.

When  $O_3$  concentrations were high in the field study, the cities under observation were surrounded with an atmosphere more comparable to the contents of the smog chambers on the second or third day of a run. A great difference in the behavior of the two systems (urban and chamber) is that no additional reactants were added to the chambers after the initial charge. Urban air, on the other hand, even when moving into rural areas, continually receives fresh reactants.

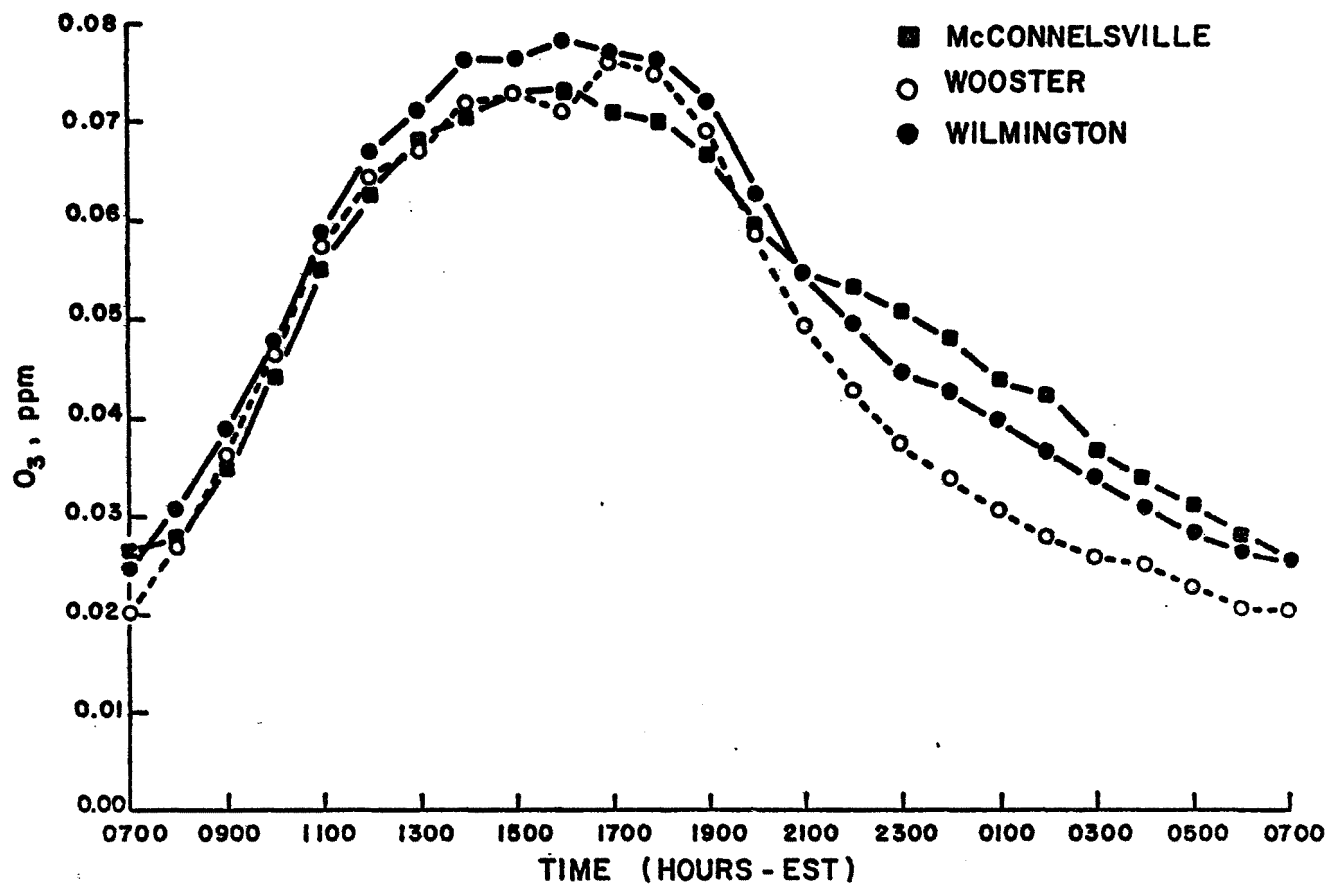


Figure 12. Mean diurnal  $O_3$  concentration at Wilmington, Wooster, and McConnelville, Ohio, from June 14-August 31, 1974.

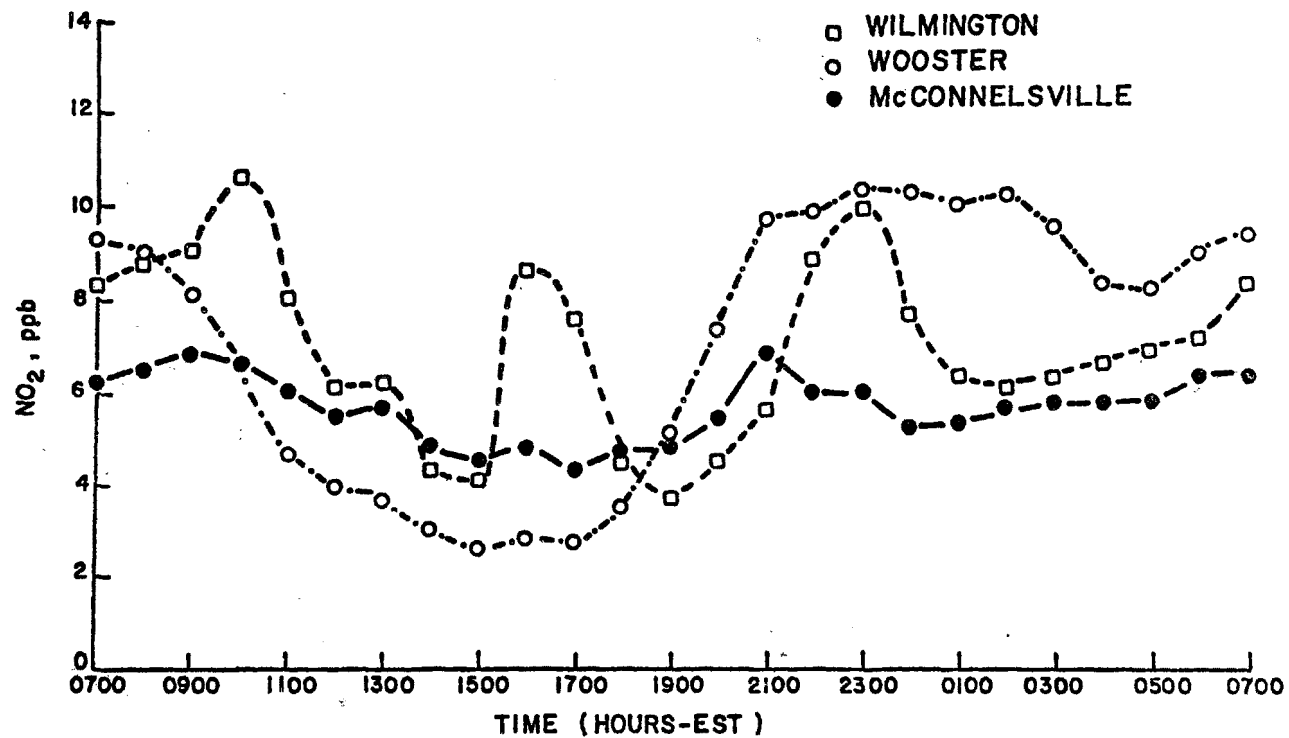


Figure 13. Mean diurnal  $\text{NO}_2$  concentration at Wilmington, Wooster, and McConnelville, Ohio, from June 14-August 31, 1974.

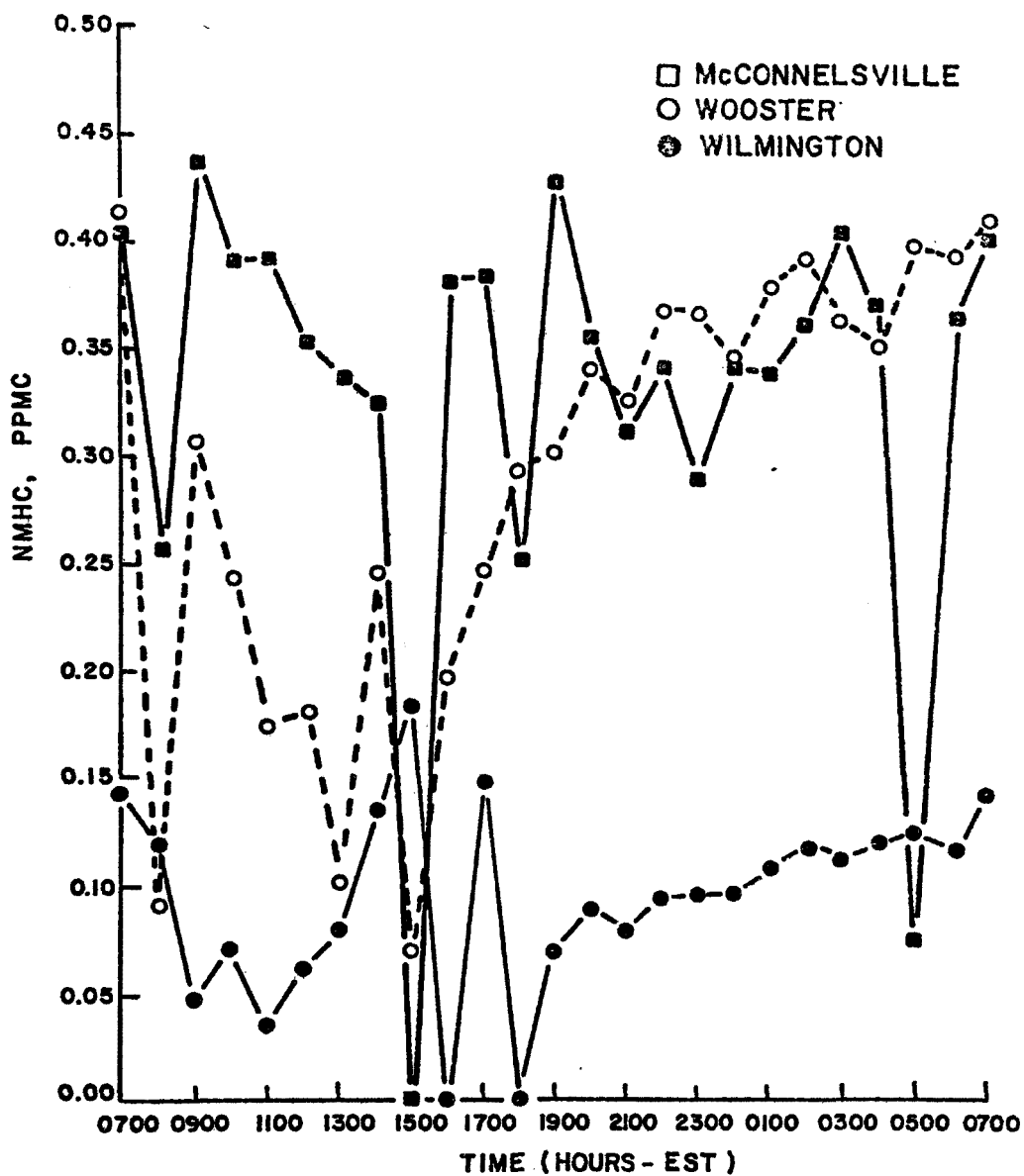


Figure 14. Mean diurnal NMHC concentration at Wilmington, Wooster, and McConnelsville, Ohio, from June 14-August 31, 1974.

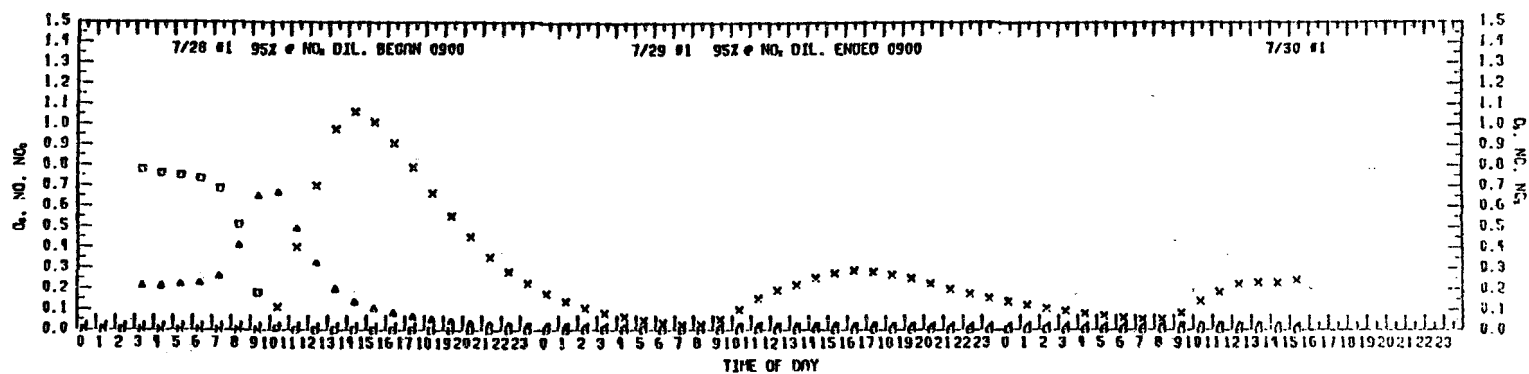


Figure 15. Typical three-day profiles for NO (□), NO<sub>2</sub> (Δ), and O<sub>3</sub> (×).

The closeness of the analogy between field data and second- and third-day chamber data, however, is surprisingly good. The average hourly concentrations of  $\text{NO}_2$  at sunrise at five rural field sites were 5, 6, 6, 7, and 8 ppb. The chamber  $\text{NO}_x$  concentrations (only  $\text{NO}_2$  was at concentrations high enough to register on the instrument) ranged from a measured 1 ppb to 39 ppb at sunrise on the second and third days of irradiation. Field NMHC concentrations at sunup at three stations were 0.15, 0.49 and 0.54 ppmC. Hydrocarbon/ $\text{NO}_x$  ratios were  $25 \frac{0.15}{.006}$ ,  $61 \frac{0.49}{.008}$ ,  $108 \frac{.54}{.005}$ .

Most second- and third-day irradiations generated  $\text{O}_3$  at concentrations above the NAAQS in the smog chambers. Examples of second- and third-day chamber data comparable to rural observations were:  $\frac{0.52}{0.014} \frac{\text{NMHC}}{\text{NO}_x}$  (ratio 37) at sunrise producing a  $\Delta\text{O}_3$  of 0.18 ppm;  $\frac{0.58}{0.007}$  (ratio 83) producing a  $\Delta\text{O}_3$  of 0.12 ppm; and  $\frac{0.47}{0.004}$  (ratio 117) producing a  $\Delta\text{O}_3$  of 0.12 ppm.

The point of the above comparison is that  $\text{O}_3$  in concentrations above the NAAQS can be generated in smog chambers from precursor concentrations (and ratios) similar to those found in the rural high  $\text{O}_3$  situations.

Urban nocturnal concentrations were considerably higher at the rural sites than at the urban sites. Except when actual mechanical dilution was taking place, smog chamber  $\text{O}_3$  concentrations never reached a measured zero at night. The explanation is that urban sources of NO are great enough to destroy the  $\text{O}_3$  at night, while rural sources of  $\text{O}_3$ -destructive gases are too weak to destroy all the  $\text{O}_3$ . Thus, reduced levels of  $\text{O}_3$ -destructive precursors and reactive intermediates permit the overnight reduction of more than half of the chamber's  $\text{O}_3$ .

The retention of  $\text{O}_3$  in nocturnal air is of importance in the total phenomenon of high  $\text{O}_3$  concentrations in rural atmospheres. The smog chamber data obtained in this study can be used to begin to quantify the persistence of high nighttime  $\text{O}_3$  concentrations in layers of air aloft in the lower troposphere. (See the previous discussion of nocturnal  $\text{O}_3$  half-lives.)

Although the olefinic content of rural air was low, there was enough olefinic material to show that the sampled air had continually received fresh precursors. The olefinic concentration of the chamber air on the second and third day of irradiation is shown in Appendix A. Reduced olefinic content allows the accumulation of  $\text{O}_3$  at low concentrations of  $\text{NO}_x$  and reduces the  $\text{O}_3$ -destructive capacity of the air.

In the RTI field study the  $\text{NO}_2$  concentrations were low (e.g., hourly averages 1 to 10 ppb) and, as can be seen in Figure 13, there was little diurnal variation. Earlier studies involving high rural  $\text{O}_3$  often did not report  $\text{NO}_x$  concentrations except to say they were "very low" (ref. 6).

In the chamber studies, the  $\text{NO}_2$  concentrations "bottomed out" but never disappeared. These low  $\text{NO}_2$  concentrations ranged from 1 to 39 ppb. While this might be construed to be an effect of chamber contamination by the original  $\text{NO}_x$  charge, it duplicates, on the second and third days of irradiation, the conditions observed in the field. The actual chemistry by which measureable concentrations of  $\text{NO}_2$  could be maintained in the face of oxidation by  $\text{O}_3$  and other oxidizing agents is not clear, but is sometimes speculated as being due to photolysis of nitroxy compounds other than nitrates. In the field it has been assumed to be due to continued low-level emissions. In chambers it has been assumed to be due to material sorbed by the walls at high initial reactant concentrations and desorbed later. In any event, the condition in the chambers simulated that in the field and may well represent some sort of cyclic gas-phase process in both cases.

Data from the RTI field study provide evidence which may indicate that local emissions were the major cause of the diurnal variation observed at rural sites. In the nocturnal radiation inversion these emissions may be equally as important as contact with the ground in causing the nighttime decrease of  $\text{O}_3$ . In the mornings they may mix with  $\text{O}_3$  and the stable intermediates of the  $\text{O}_3$  generation to form a system capable of  $\text{O}_3$  generation. This interpretation is consistent with the vertical  $\text{O}_3$  soundings depicted in Figure 10. The indicated diurnal  $\text{O}_3$  curve between 600 and 1200 m is much shallower than the diurnal curve at ground level. This was interpreted as indicating that the air aloft, between 600 and 1200 m, had little  $\text{O}_3$ -generative or -destructive capacity. The fact that on the second and third day  $\text{O}_3$  exhibits a diurnal curve in the chambers, where there were no added reactants, casts doubts on the assumed necessity of having local emissions. In other words, an "aged" photochemical system may contain sufficient  $\text{O}_3$ -generative capacity to exceed the standard. On the other hand, local pollutants, when present, will enter into both  $\text{O}_3$ -destruction and -generation processes.

Although the interpretation of field data may be correct, the "spent" photochemical system in the chamber is capable of considerable  $O_3$  generation on second and third days of irradiation without the introduction of additional precursors or intermediates. The implication of this is that generation of  $O_3$  and diurnal behavior similar to that observed in the field can, and in some cases may, occur in air drifting downwind of a city without any local emissions affecting the results.



## REFERENCES

1. U.S. Environmental Protection Agency, 1971. Air Quality Criteria for Nitrogen Oxides. Air Pollution Control Office Publication No. AP-84.
2. Intersociety Committee, Procedure 403, 1972. Methods of Air Sampling and Analysis. American Public Health Association, Washington, D.C.
3. Intersociety Committee, Procedure 110, 1972. Methods of Air Sampling and Analysis. American Public Health Association, Washington, D.C.
4. Fox, D. L., Kamens, R., and Jeffries, H. E., 1975. Photochemical Smog Systems: Effect of Dilution on Ozone. Science, 188:No. 4193, p. 1113.
5. Research Triangle Institute, 1975. Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies. Environmental Protection Agency Publication No. EPA-450/3-75-036.
6. Research Triangle Institute, 1974. Investigation of Ozone and Ozone Precursor Concentrations at Nonurban Locations in the Eastern United States. Environmental Protection Agency Publication No. EPA-450/3-74-034.

## APPENDIXES

### Appendix A. INDIVIDUAL HYDROCARBON ANALYSES

Compound
Ethylene, ppbC
Propane, ppbC
Propylene, ppbC
Acetylene, ppbC
n-Butane, ppbC
1-Butene, ppbC
trans-2-Butene, ppbC
Isopentane, ppbC
Cyclopentane, ppbC
2-Methyl-2-Butene, ppbC
Toluene, ppbC
ortho-Xylene, ppbC
THC, ppmC
Methane, ppmC
Carbon Monoxide, ppmC
NMHC, ppmC

\* In selected cases where analytical data are not available, estimates were made. Estimated concentrations are enclosed by parentheses.

Dilution 95%, Initiated at 1700      Dates: 7/22 - 7/24/75

Chamber No. 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0508	1616	0536	1706	0533	1646
Ethylene	—	116.8	3.85	3.7	2.09	1.08
Propane	—	369.0	23.03	21.39	18.82	11.43
Propylene	—	9.21	(3.0)	1.85	1.61	1.49
Acetylene	—	2.6	0.0	0.0	0.45	0.11
n-Butane	—	696.0	37.34	35.48	30.20	10.44
1-Butene	—	1.36	0.0	(0.0)	0.0	0.0
trans-2-Butene						
Isopentane	—	331.5	14.72	16.75	11.72	3.47
Cyclopentane	—	8.25	0.0	0.29	0.0	0.40
2-Methyl-2-Butene						
Toluene	—	—	—	—	—	—
ortho-Xylene						
THC (ppm)	11.55	5.16	1.83	1.36	1.27	1.33
Methane	0.10	0.16	0.06	0.16	0.20	0.27
Carbon Monoxide	8.59	9.10	1.48	0.39	0.31	0.43
NMHC	11.45	5.00	1.78	1.20	1.07	1.07

Dilution 95%, Initiated at 1700 Dates: 7/22 - 7/24/75

Chamber No. 2

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0518	1631	0544	1716	0541	1656
Ethylene	—	26.3	2.25	1.86	1.55	0.94
Propane	—	72.9	8.96	4.86	3.12	1.44
Propylene	—	1.19	0.16	0.59	0.47	0.43
Acetylene	—	0.33	0.0	0.0	0.0	0.0
n-Butane	—	342.80	9.52	9.84	8.57	2.96
1-Butene	—	0.0	0.0	0.0	0.0	0.0
trans-2-Butene						
Isopentane	—	227.5	4.73	4.93	3.54	5.35
Cyclopentane	—	6.0	0.0	0.0	0.0	0.0
2-Methyl-2-Butene						
Toluene	—	—	—	—	—	—
ortho-Xylene						
THC	4.94	3.69	1.46	1.24	1.15	1.16
Methane	0.47	0.50	0.162	0.25	0.21	0.25
Carbon Monoxide	9.60	9.95	1.16	0.24	0.21	0.37
NMHC	4.47	3.20	1.30	0.99	0.94	0.91

Dilution 95%, Initiated at 1700

Dates: 7/22 - 7/24/75

Chamber No. 3

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0528	1728	0553	1731	0550	1711
Ethylene	—	—	2.13	2.62	3.08	4.54
Propane	—	—	6.48	5.58	3.26	3.45
Propylene	—	—	0.23	0.66	1.25	0.69
Acetylene	—	—	0.0	0.0	0.64	0.54
n-Butane	—	—	7.91	9.84	14.94	2.91
1-Butene	—	—	0.07	0.0	0.60	0.0
trans-2-Butene						
Isopentane	—	—	4.29	3.25	8.76	7.45
Cyclopentane	—	—	0.0	0.0	0.0	0.0
2-Methyl-2-Butene						
Toluene	—	—	—	—	—	—
ortho-Xylene						
THC	4.71	3.32	1.28	1.14	1.10	—
Methane	0.60	0.60	0.10	0.22	0.22	—
Carbon Monoxide	8.90	8.44	1.19	0.26	0.21	—
NMHC	4.11	2.73	1.18	0.93	0.89	—

Dilution 95%, Initiated at 1700

Dates: 7/22 - 7/24/75

Chamber No. 4

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0558	1650	0559	1600	0557	1726
Ethylene	—	5.62	1.81	3.40	1.30	2.06
Propane	—	16.47	2.51	1.31	0.23	0.80
Propylene	—	0.23	0.0	0.39	0.36	0.59
Acetylene	—	0.11	0.0	0.0	0.14	0.20
n-Butane	—	38.32	5.66	2.62	2.52	1.10
1-Butene	—	0.0	0.0	0.0	0.0	0.12
trans-2-Butene						
Isopentane	—	17.25	3.07	1.27	2.49	0.16
Cyclopentane	—	0.0	0.0	0.0	0.0	0.0
2-Methyl-2-Butene						
Toluene	—	—	—	—	—	—
ortho-Xylene						
THC	2.14	1.89	1.22	1.31	1.21	1.20
Methane	0.38	0.45	0.28	0.49	0.49	0.44
Carbon Monoxide	10.00	9.21	0.85	0.18	0.18	0.27
NMHC	1.76	1.45	0.95	0.82	0.72	0.76

Dilution 95%, Initiated at  
 NO<sub>x</sub> Crossover

Dates: 7/28 - 7/30/75

Chamber No. 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0501	1701	0538	1738	0536	1538
Ethylene	(660)	37.20	1.78	—	1.82	—
Propane	660.0	275.10	9.63	—	8.96	—
Propylene	309.0	15.42	0.26	—	0.38	—
Acetylene	1184.0	143.20	7.70	—	6.60	—
n-Butane	2344.0	616.0	16.66	—	11.38	—
1-Butene	152.4	0.0	0.0	—	0.0	—
trans-2-Butene						
Isopentane	1965.0	331.50	6.70	—	4.31	—
Cyclopentane	(79)	8.05	0.0	—	0.0	—
2-Methyl-2-Butene						
Toluene	—	—	—	—	—	—
ortho-Xylene						
THC	7.52	2.10	0.98	0.70	—	0.91
Methane	0.50	0.25	0.14	0.13	—	0.15
Carbon Monoxide	9.05	2.96	0.53	0.44	—	0.57
NMHC	7.02	1.85	0.84	0.57	—	0.81

Dilution 95%, Initiated at  
NO<sub>x</sub> Crossover

Dates: 7/28 - 7/30/75

Chamber No. 2

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0517	1711	0545	1748	0544	1548
Ethylene	270.01	4.22	2.22	—	1.43	—
Propane	188.10	9.63	4.35	—	1.58	—
Propylene	420.0	0.0	0.35	—	0.35	—
Acetylene	130.80	0.40	0.0	—	0.0	—
n-Butane	1348.0	20.92	10.58	—	4.72	—
1-Butene	58.80	0.0	0.0	—	0.0	—
trans-2-Butene						
Isopentane	1025.0	12.65	2.42	—	1.30	—
Cyclopentane	26.70	0.0	0.0	—	0.0	—
2-Methyl-2-Butene						
Toluene	—	—	—	—	—	—
ortho-Xylene						
THC	4.81	1.50	1.07	0.87	—	0.99
Methane	0.57	0.47	0.35	0.20	—	0.32
Carbon Monoxide	10.00	2.29	0.22	0.24	—	0.38
NMHC	4.24	1.03	0.72	0.67	—	0.66



Dilution 95%, Initiated at  
NO<sub>x</sub> Crossover

Dates: 7/28 - 7/30/75

Chamber No. 3

Compound	Time of Sample					
	Day 1 0527 1731		Day 2 0554 1758		Day 3 0552 1558	
Ethylene	(384)	4.56	2.12	—	5.42	—
Propane	384.0	15.81	3.80	—	3.50	—
Propylene	117.30	0.32	0.51	—	0.55	—
Acetylene	596.0	0.0	0.0	—	0.66	—
n-Butane	1240.0	48.4	7.32	—	4.68	—
1-Butene	100.0	0.0	0.0	—	0.0	—
trans-2-Butene						
Isopentane	935.0	21.25	3.63	—	3.31	—
Cyclopentane	(37)	0.0	0.0	—	0.0	—
2-Methyl-2-Butene						
Toluene	—	—	—	—	—	—
ortho-Xylene						
THC	4.05	1.07	0.60	0.35	—	0.66
Methane	0.10	0.09	0.08	0.10	—	0.10
Carbon Monoxide	8.93	2.55	0.31	0.33	—	0.43
NMHC	3.95	0.98	0.52	0.25	—	0.56

Dilution 95%, Initiated at  
NO<sub>x</sub> Crossover

Dates: 7/28 - 7/30/75

Chamber No. 4

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0536	1731	0603	1828	0602	1628
Ethylene	98.48	5.50	1.04	—	3.13	—
Propane	82.35	15.18	0.66	—	1.11	—
Propylene	40.50	0.61	0.22	—	0.41	—
Acetylene	10.30	0.31	0.0	—	0.21	—
n-Butane	278.60	39.24	3.67	—	1.34	—
1-Butene	19.88	0.32	0.0	—	0.0	—
trans-2-Butene						
Isopentane	211.95	22.40	1.48	—	0.86	—
Cyclopentane	7.05	0.45	0.0	—	0.0	—
2-Methyl-2-Butene						
Toluene	—	—	—	—	—	—
Ortho-Xylene						
THC	2.05	1.25	1.00	0.94	—	1.15
Methane	0.90	0.65	0.40	0.41	—	0.58
Carbon Monoxide	10.00	2.02	0.20	0.23	—	0.34
NMHC	1.15	0.60	0.60	0.53	—	0.57

Dilution 77%, Initiated at  
NO<sub>x</sub> Crossover

Dates; 8/4 - 8/6/75

Chamber No. 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0559	1801	0537	1601	0538	1638
Ethylene	8.82	1.10	0.58	0.0	—	—
Propane	12.75	2.64	4.83	0.96	—	—
Propylene	5.58	0.0	0.0	0.0	—	—
Acetylene	13.28	4.12	4.64	1.98	—	—
n-Butane	59.6	6.56	4.76	0.94	—	—
1-Butene	46.0	0.0	0.0	0.0	—	—
trans-2-Butene						
Isopentane	31.0	3.27	1.33	0.0	—	—
Cyclopentane	0.0	0.0	0.0	0.0	—	—
2-Methyl-2-Butene						
Toluene	770.0	183.4	144.2	21.07	—	—
ortho-Xylene						
THC	7.47	2.16	1.18	0.79	0.94	0.85
Methane	0.12	0.11	0.15	0.11	0.15	0.24
Carbon Monoxide	9.03	4.51	1.74	1.34	1.35	1.35
NMHC	7.35	2.05	1.03	0.68	0.79	0.67

Dilution 77%, Initiated at  
 NO<sub>x</sub> Crossover

Dates: 8/4 - 8/6/75

Chamber 2

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0542	1811	0546	1611	0548	1648
Ethylene	7.82	0.62	0.43	0.27	—	—
Propane	12.57	0.73	—	0.36	—	—
Propylene	6.09	0.0	0.0	0.23	—	—
Acetylene	10.18	0.82	—	0.38	—	—
n-Butane	41.20	2.30	1.82	0.61	—	—
1-Butene	3.04	0.0	0.0	0.0	—	—
trans-2-Butene						
Isopentane	31.45	3.83	0.0	0.0	—	—
Cyclopentane	0.0	0.0	0.0	0.0	—	—
2-Methyl-2-Butene						
Toluene	1000.	124.6	67.87	8.89	—	—
ortho-Xylene						
THC	5.19	1.84	1.16	0.91	1.00	0.99
Methane	0.78	0.38	0.27	0.33	0.38	0.36
Carbon Monoxide	9.84	4.61	1.62	1.18	1.17	1.21
NMHC	4.41	1.46	0.89	0.58	0.62	0.63

Dilution 77%, Initiated at  
NO<sub>x</sub> Crossover

Dates: 8/4 - 8/6/75

Chamber 3

Compound	Time of Sample					
	Day 1 0658 1821		Day 2 0554 1658		Day 3 0558 1658	
Ethylene	—	1.85	0.37	—	—	—
Propane	—	8.46	1.75	—	—	—
Propylene	—	0.0	0.13	—	—	—
Acetylene	—	16.10	3.29	—	—	—
n-Butane	—	17.92	2.99	—	—	—
1-Butene	—	0.0	0.0	—	—	—
trans-2-Butene						
Isopentane	—	6.55	1.68	—	—	—
Cyclopentane	—	0.0	0.0	—	—	—
2-Methyl-2-Butene						
Toluene	—	156.8	1.32	—	—	—
ortho-Xylene						
THC (ppm)	4.50	1.59	0.83	0.71	0.81	0.84
Methane	0.11	0.15	0.22	0.09	0.24	0.34
Carbon Monoxide	9.03	3.86	1.28	0.96	0.89	0.89
NMHC	4.40	1.44	0.61	0.62	0.58	0.50

Dilution 77%, Initiated at  
NO<sub>x</sub> Crossover

Dates: 8/4 - 8/6/75

Chamber No. 4

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0559	1831	0603	1631	0608	1608
Ethylene	1.63	0.31	0.51	0.0	—	—
Propane	3.0	1.79	0.56	0.0	—	—
Propylene	1.32	0.0	0.33	0.0	—	—
Acetylene	3.70	4.16	0.42	0.72	—	—
n-Butane	12.40	3.14	1.56	0.0	—	—
1-Butene	0.0	0.0	0.17	0.0	—	—
trans-2-Butene						
Isopentane	12.25	0.27	1.73	0.0	—	—
Cyclopentane	0.0	0.0	0.0	0.0	—	—
2-Methyl-2-Butene						
Toluene	295.4	50.82	0.0	0.0	—	—
ortho-Xylene						
THC (ppm)	1.14	0.65	0.67	0.70	0.70	0.73
Methane	0.14	0.10	0.17	0.06	0.26	0.35
Carbon Monoxide	10.34	3.87	1.33	1.04	0.93	0.89
NMHC	1.00	0.54	0.49	0.64	0.44	0.38

Dilution 77%, Initiated at  
NO<sub>x</sub> Crossover

Dates: 8/8 - 8/10/75

Chamber No. 1

Compound	Time of Sample				
	Day 1		Day 2		Day 3
	0536	1731	0535	1540	0535
Ethylene	582.74	57.40	15.08	6.81	5.52
Propane	542.71	291.0	94.50	44.41	34.50
Propylene	197.90	9.54	2.24	1.49	1.03
Acetylene	744.01	312.0	95.00	49.66	30.40
n-Butane	1637.50	610.0	186.0	50.36	32.92
1-Butene	116.32	1.08	0.0	0.0	0.0
trans-2-Butene					
Isopentane	1152.40	324.0	95.50	21.16	17.30
Cyclopentane	27.28	7.25	2.11	0.45	0.0
2-Methyl-2-Butene					
Toluene	2021.5	625.10	(200)	59.99	58.45
ortho-Xylene					
THC (ppm)	7.05	3.28	2.10	—	1.72
Methane	1.23	1.19	1.18	—	1.20
Carbon Monoxide	8.48	5.13	1.79	—	1.31
NMHC	5.81	2.09	0.92	—	0.52

Dilution 77%, Initiated at  
 NO<sub>x</sub> Crossover

Dates: 8/8 - 8/10/75

Chamber No. 2

Compound	Time of Sample				
	Day 1		Day 2		Day 3
	0546	1741	0543	1551	0543
Ethylene	288.15	26.60	10.88	1.74	2.54
Propane	294.89	122.70	42.30	12.06	10.59
Propylene	104.61	3.24	1.31	0.96	0.36
Acetylene	452.0	168.20	50.80	12.57	13.26
n-Butane	830.69	255.20	86.40	15.25	12.96
1-Butene	47.76	0.22	—	0.0	0.0
trans-2-Butene					
Isopentane	535.16	134.50	46.15	9.82	6.60
Cyclopentane	14.42	3.21	1.12	0.0	0.0
2-Methyl-2-Butene					
Toluene	1308.30	390.60	200.20	41.86	22.40
ortho-Xylene					
THC (ppm)	3.64	1.39	0.72	—	0.69
Methane	0.13	0.11	0.20	—	0.07
Carbon Monoxide	10.25	4.99	1.45	—	0.97
NMHC	3.52	1.28	0.52	—	0.62



Dilution 77%, Initiated at  
NO<sub>x</sub> Crossover

Dates: 8/8 - 8/10/75

Chamber No. 3

Compound	Time of Sample				
	Day 1 0552      1748		Day 2 0552      1556		Day 3 0551
Ethylene	249.73	36.40	11.58	3.63	6.40
Propane	249.53	98.70	42.0	11.19	17.01
Propylene	92.70	1.88	1.76	1.06	1.02
Acetylene	315.68	115.20	44.20	10.68	13.94
n-Butane	731.56	230.40	87.60	13.97	14.68
1-Butene	38.94	0.36	0.0	0.0	0.0
trans-2-Butene					
Isopentane	458.35	129.0	46.55	7.36	7.30
Cyclopentane	12.27	4.24	0.97	0.0	0.0
2-Methyl-2-Butene					
Toluene	1050.20	196.70	108.50	36.33	25.62
ortho-Xylene					
THC (ppm)	3.24	1.38	0.69	—	0.91
Methane	0.15	0.10	0.14	—	0.07
Carbon Monoxide	8.80	4.41	1.33	—	0.86
NMHC	3.09	1.28	0.55	—	0.84

Dilution 77%, Initiated at  
NO<sub>x</sub> Crossover

Dates: 8/8 - 8/10/75

Chamber No. 4

Compound	Time of Sample				
	Day 1 0600 1751		Day 2 0602 1606		Day 3 0600
Ethylene	61.70	10.12	4.46	5.36	3.14
Propane	54.22	26.31	8.04	4.54	2.81
Propylene	20.21	1.50	0.35	1.39	0.38
Acetylene	39.78	18.50	6.12	1.24	1.88
n-Butane	149.34	54.0	22.56	7.82	5.40
1-Butene	10.17	0.0	0.0	0.90	0.0
trans-2-Butene					
Isopentane	82.29	29.15	12.70	8.52	4.02
Cyclopentane	0.89	0.0	0.0	0.0	0.0
2-Methyl-2-Butene					
Toluene	261.10	149.80	73.50	42.0	45.22
ortho-Xylene					
THC (ppm)	1.04	0.55	0.68	—	0.99
Methane	0.11	0.13	0.13	—	0.28
Carbon Monoxide	10.46	4.92	1.53	—	1.08
NMHC	0.93	0.41	0.55	—	0.71

Dilution Static

Dates: 8/12 - 8/14/75

Chamber No. 1

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0536	1631	0538	1638	0538	1538
Ethylene	552.12	83.6	—	—	—	—
Propane	449.85	360.0	—	—	—	—
Propylene	180.71	0.0	—	—	—	—
Acetylene	415.05	336.0	—	—	—	—
n-Butane	946.52	848.0	—	—	—	—
1-Butene	112.75	0.0	—	—	—	—
trans-2-Butene						
Isopentane	1115.20	865.0	—	—	—	—
Cyclopentane	33.83	24.9	—	—	—	—
2-Methyl-2-Butene						
Toluene	2086.50	959.0	—	—	—	—
ortho-Xylene						
THC	9.02	5.93	5.05	4.33	4.23	3.82
Methane	1.29	1.14	1.22	1.22	1.20	1.27
Carbon Monoxide	8.70	8.94	9.09	8.89	8.52	8.47
NMHC	7.73	4.79	3.83	3.11	3.04	2.55

Dilution Static

Dates: 8/12 - 8/14/75

Chamber No. 2

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0545	1641	0548	1748	0548	1548
Ethylene	302.81	74.6	—	—	—	—
Propane	246.48	217.5	—	—	—	—
Propylene	92.62	3.1	—	—	—	—
Acetylene	203.90	169.8	—	—	—	—
n-Butane	538.54	384.8	—	—	—	—
1-Butene	61.74	0.0	—	—	—	—
trans-2-Butene						
Isopentane	503.78	325.0	—	—	—	—
Cyclopentane	15.51	8.8	—	—	—	—
2-Methyl-2-Butene						
Toluene	462.02	—	—	—	—	—
ortho-Xylene						
THC	4.94	3.36	3.30	2.82	2.73	2.60
Methane	0.60	0.52	0.69	0.56	0.71	0.69
Carbon Monoxide	9.50	9.61	9.89	9.58	9.30	8.93
NMHC	4.34	2.85	2.60	2.25	2.02	1.91

Dilution Static

Dates: 8/12 - 8/14/75

Chamber No. 3

Compound	Time of Sample					
	Day 1		Day 2		Day 3	
	0554	1649	0558	1758	0558	1558
Ethylene	264.14	47.2	—	—	—	—
Propane	201.61	126.0	—	—	—	—
Propylene	81.02	2.3	—	—	—	—
Acetylene	172.29	99.4	—	—	—	—
n-Butane	496.79	247.6	—	—	—	—
1-Butene	54.12	0.0	—	—	—	—
trans-2-Butene						
Isopentane	510.10	300.0	—	—	—	—
Cyclopentane	16.59	10.8	—	—	—	—
2-Methyl-2-Butene						
Toluene	851.06	497.7	—	—	—	—
ortho-Xylene						
THC	3.97	2.55	2.55	2.00	2.08	1.80
Methane	0.16	0.10	0.08	0.11	0.28	0.39
Carbon Monoxide	8.76	8.65	8.19	7.65	6.98	6.40
NMHC	3.81	2.45	2.47	1.89	1.81	1.41

Dilution Static

Dates: 8/12 - 8/14/75

Chamber No. 4

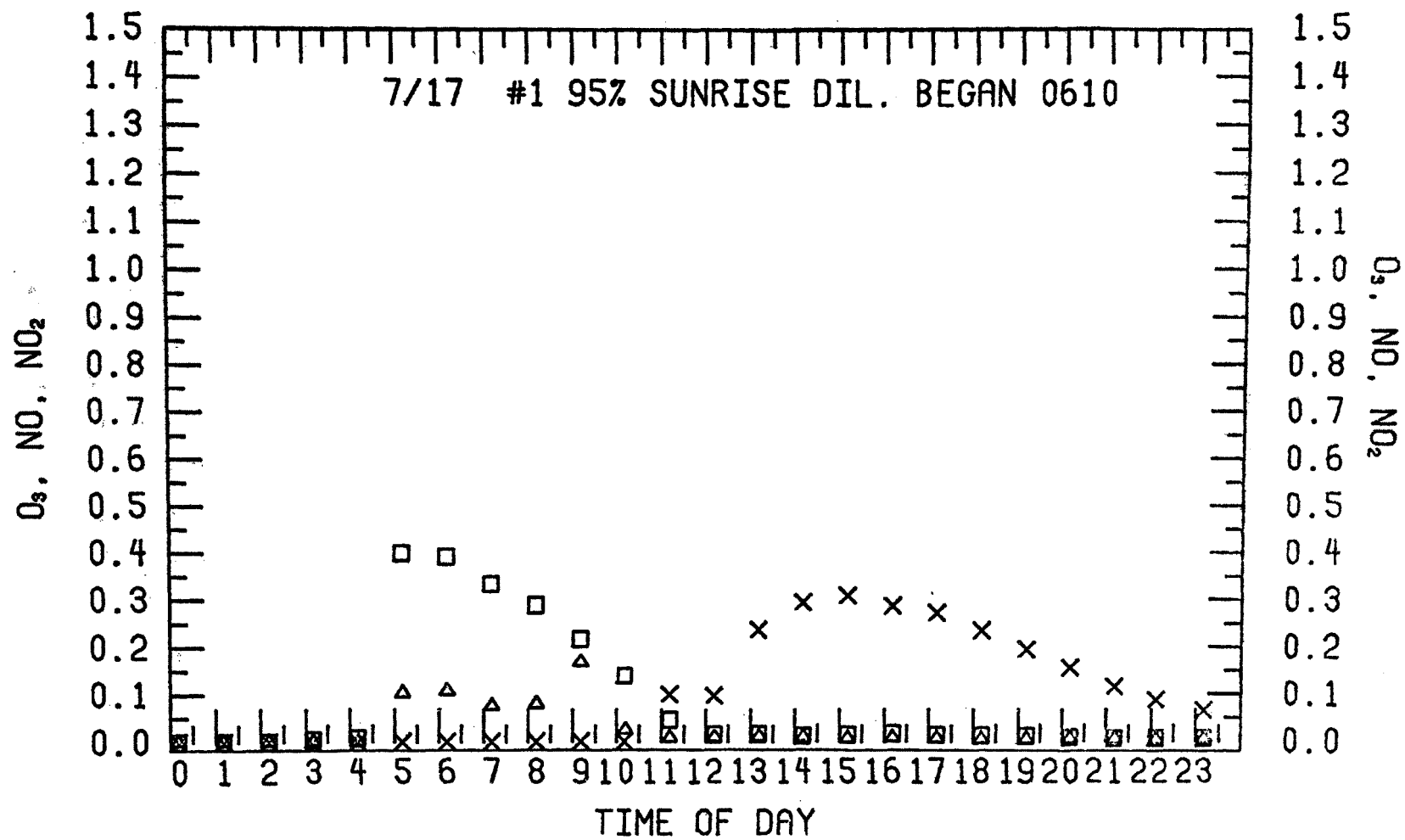
Compound	Time of Sample					
	Day 1 0602      1659		Day 2 0601      1726		Day 3 0602      1651	
Ethylene	65.51	24.40	24.78	17.64	8.71	10.56
Propane	56.77	61.20	62.81	50.72	41.22	28.52
Propylene	23.99	1.06	2.76	3.21	1.83	1.00
Acetylene	42.83	47.0	47.40	35.86	27.60	27.86
n-Butane	110.92	110.80	134.04	93.98	83.84	61.70
1-Butene	13.21	0.0	0.0	0.0	0.0	0.0
trans-2-Butene						
Isopentane	124.39	92.0	92.05	56.3	50.63	33.94
Cyclopentane	3.61	2.33	2.34	0.0	0.0	0.0
2-Methyl-2-Butene						
Toluene	276.66	—	106.69	75.91	—	53.91
ortho-Xylene						
THC	1.67	1.31	1.42	1.37	1.46	1.46
Methane	0.11	0.06	0.12	0.27	0.39	0.53
Carbon Monoxide	9.40	8.84	8.59	7.65	7.23	6.40
NMHC	1.56	1.25	1.30	1.10	1.07	0.93

## Appendix B. CONCENTRATION PROFILES

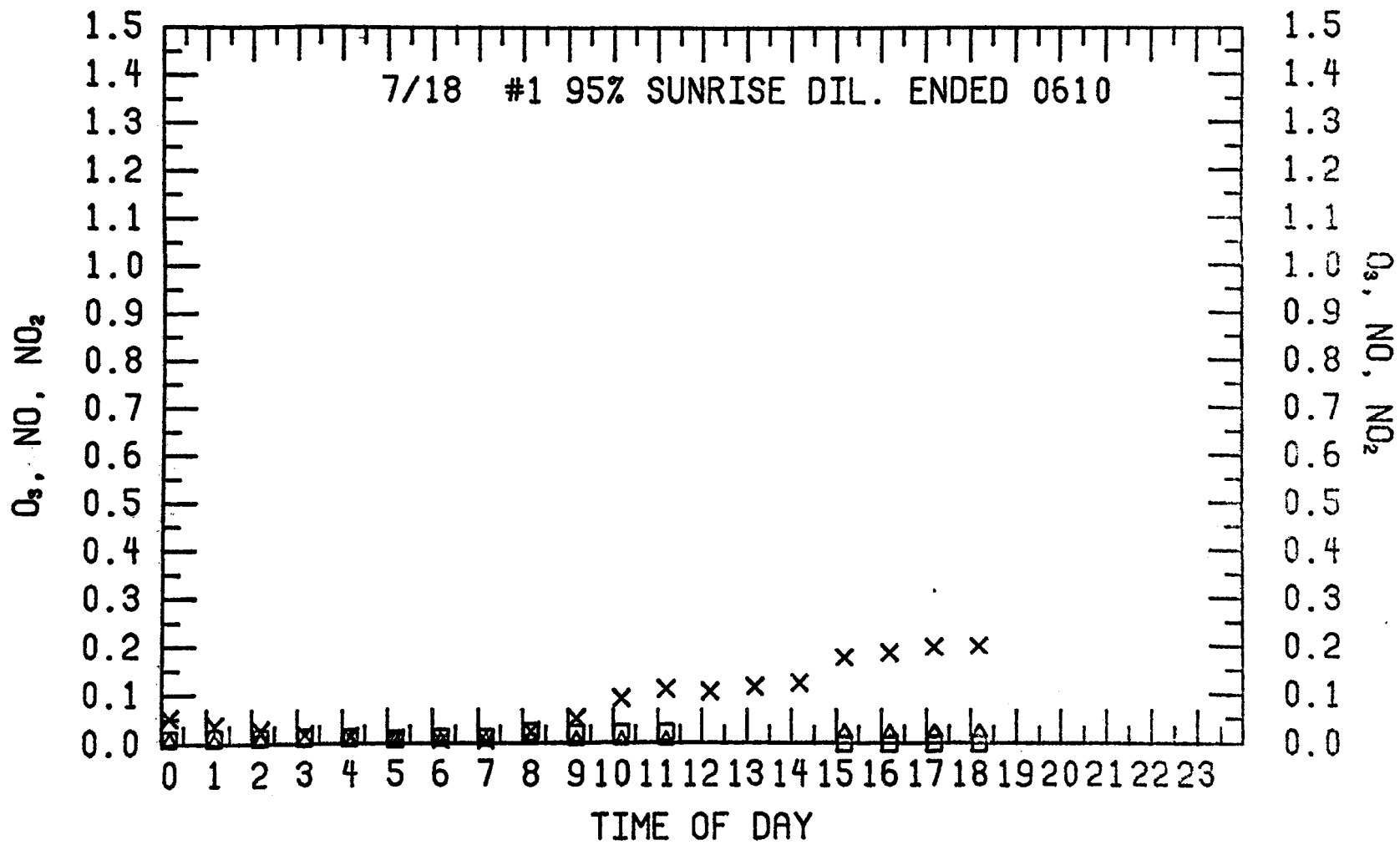
### Symbols:

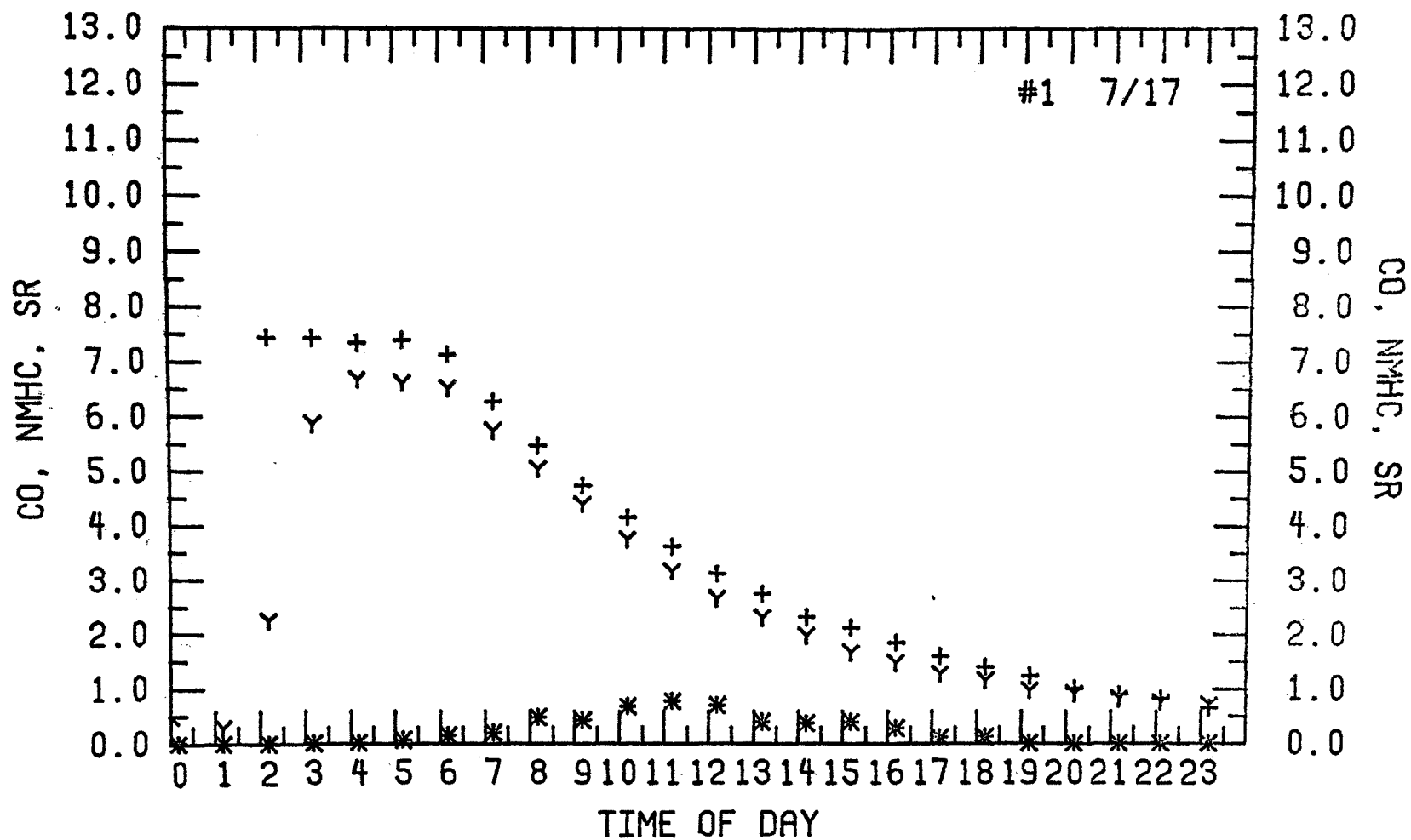
- x Ozone ppm
- Nitric Oxide ppm
- Δ Nitrogen Dioxide ppm
- + Carbon Monoxide ppm
- Y Nonmethane Hydrocarbon (ppmC)
- \* Solar Radiation (Langleys per minute)

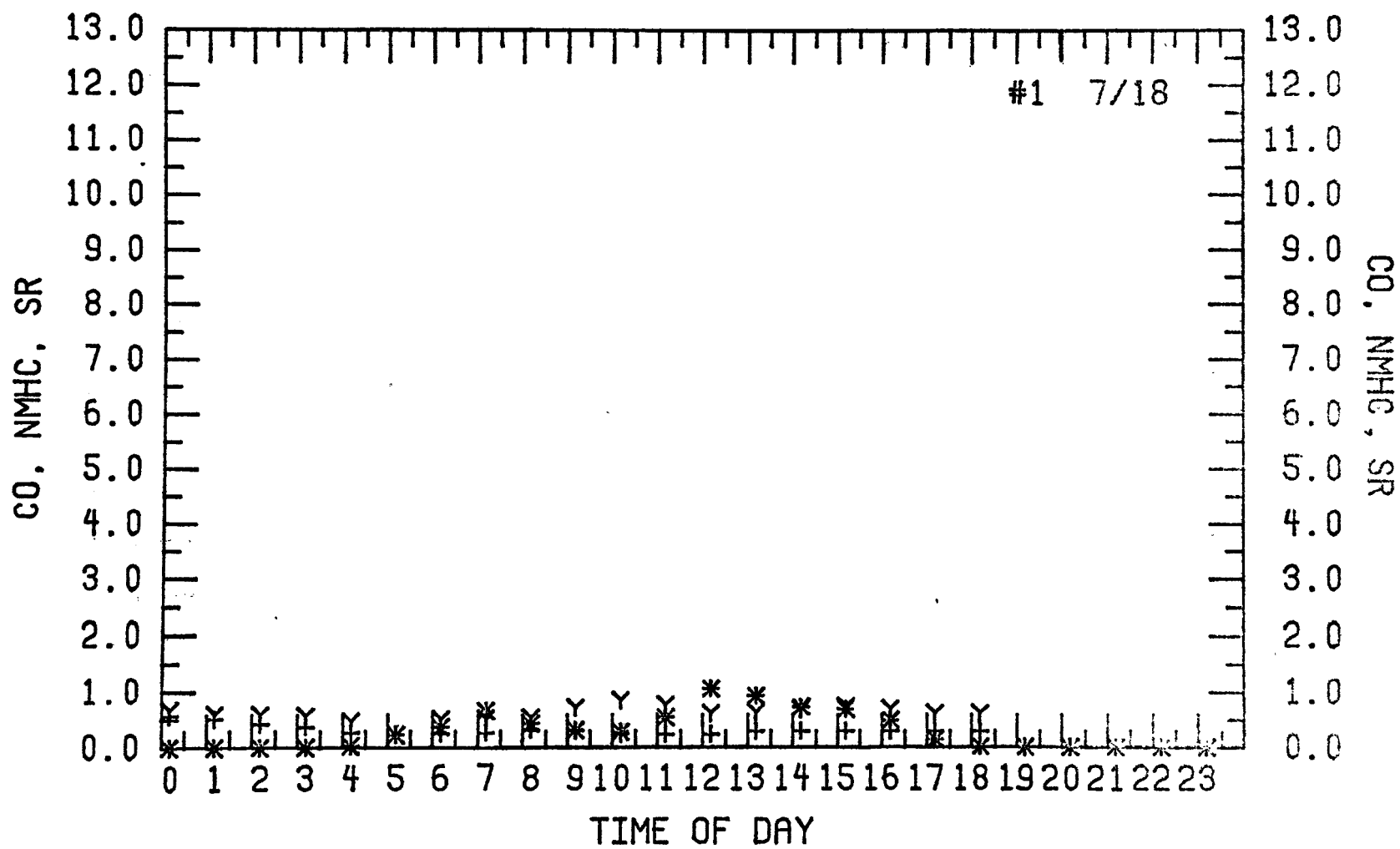
Dates, chamber numbers, percent dilution in 24 hours, and time dilution began are presented on the ozone graphs of the first two days.

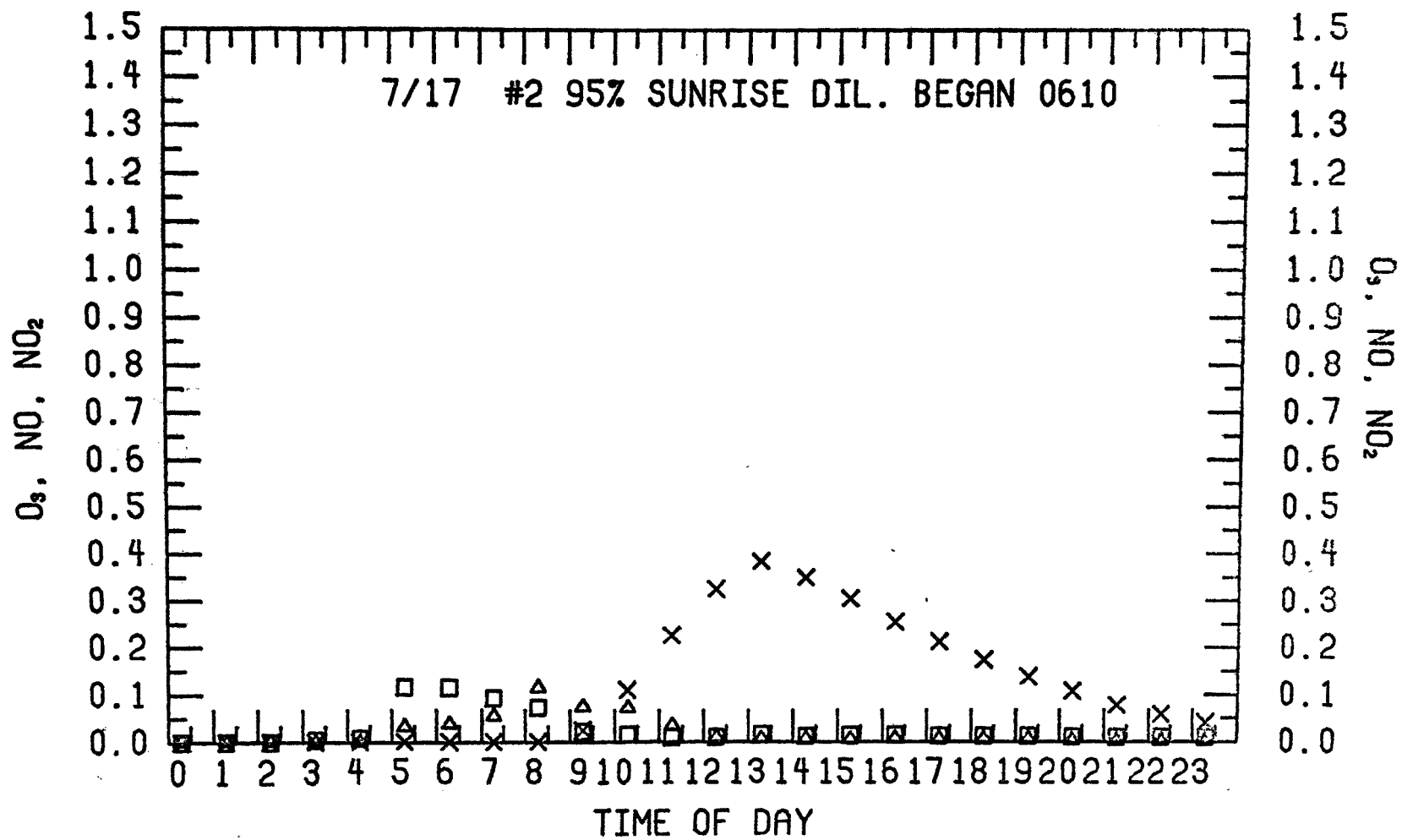


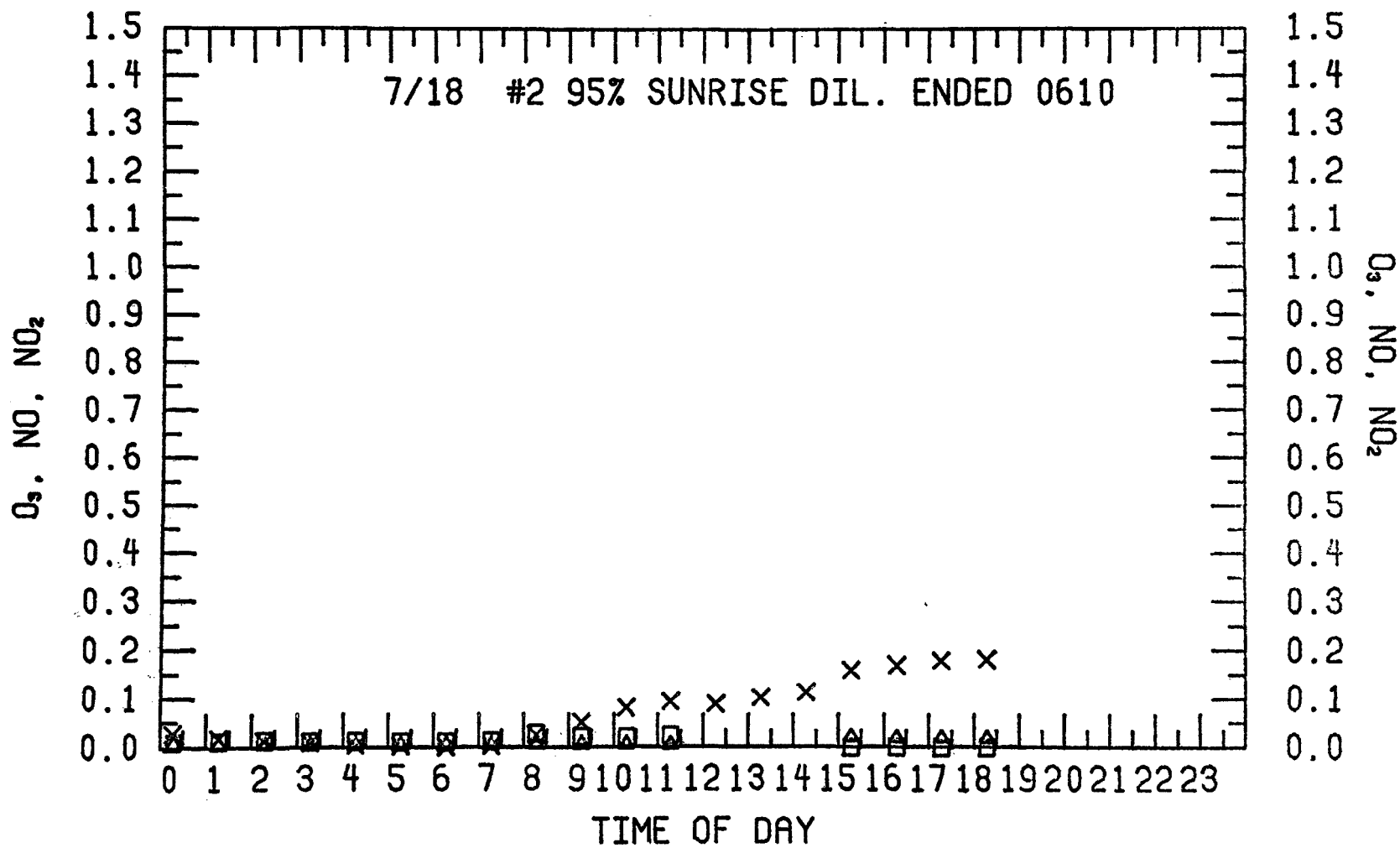


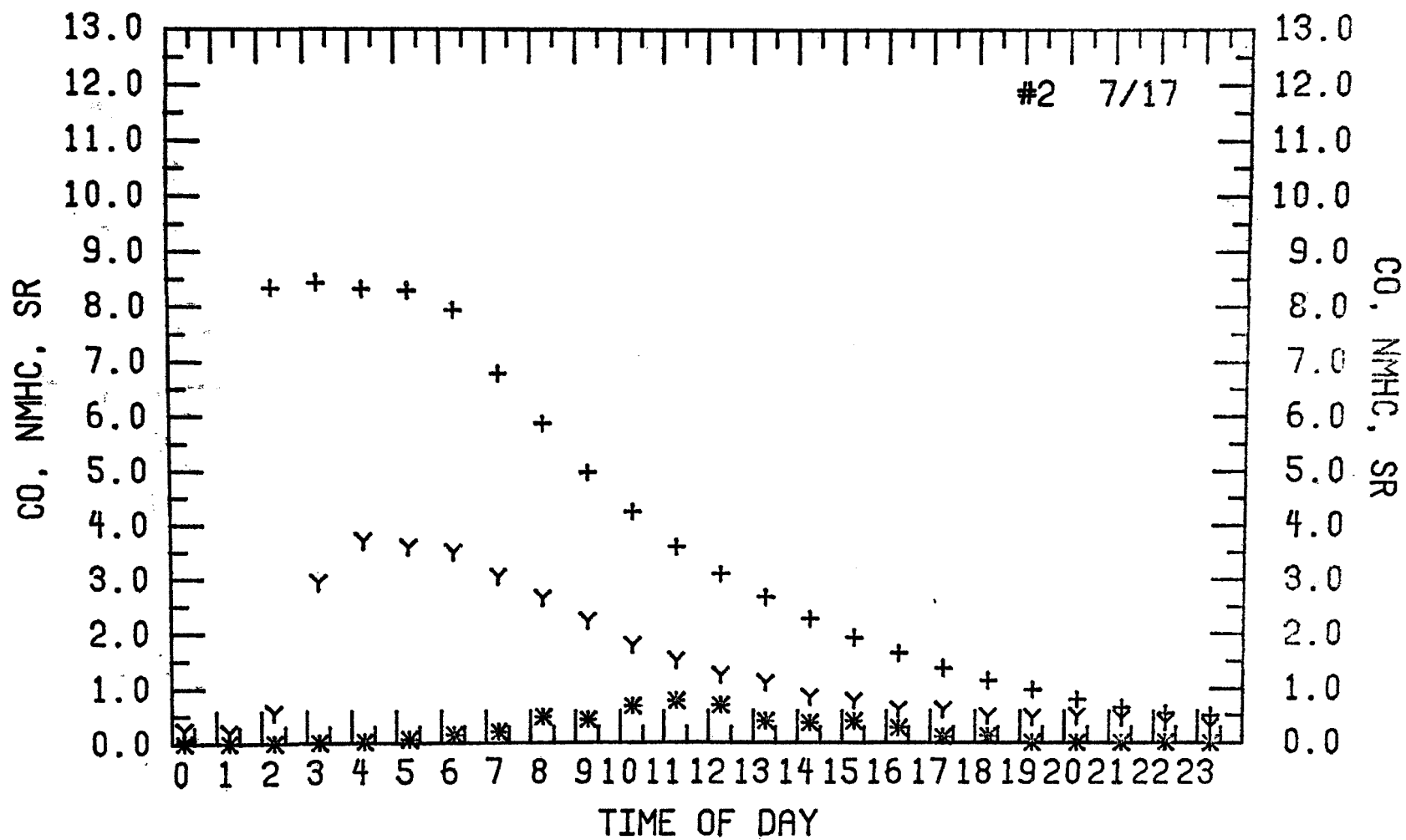


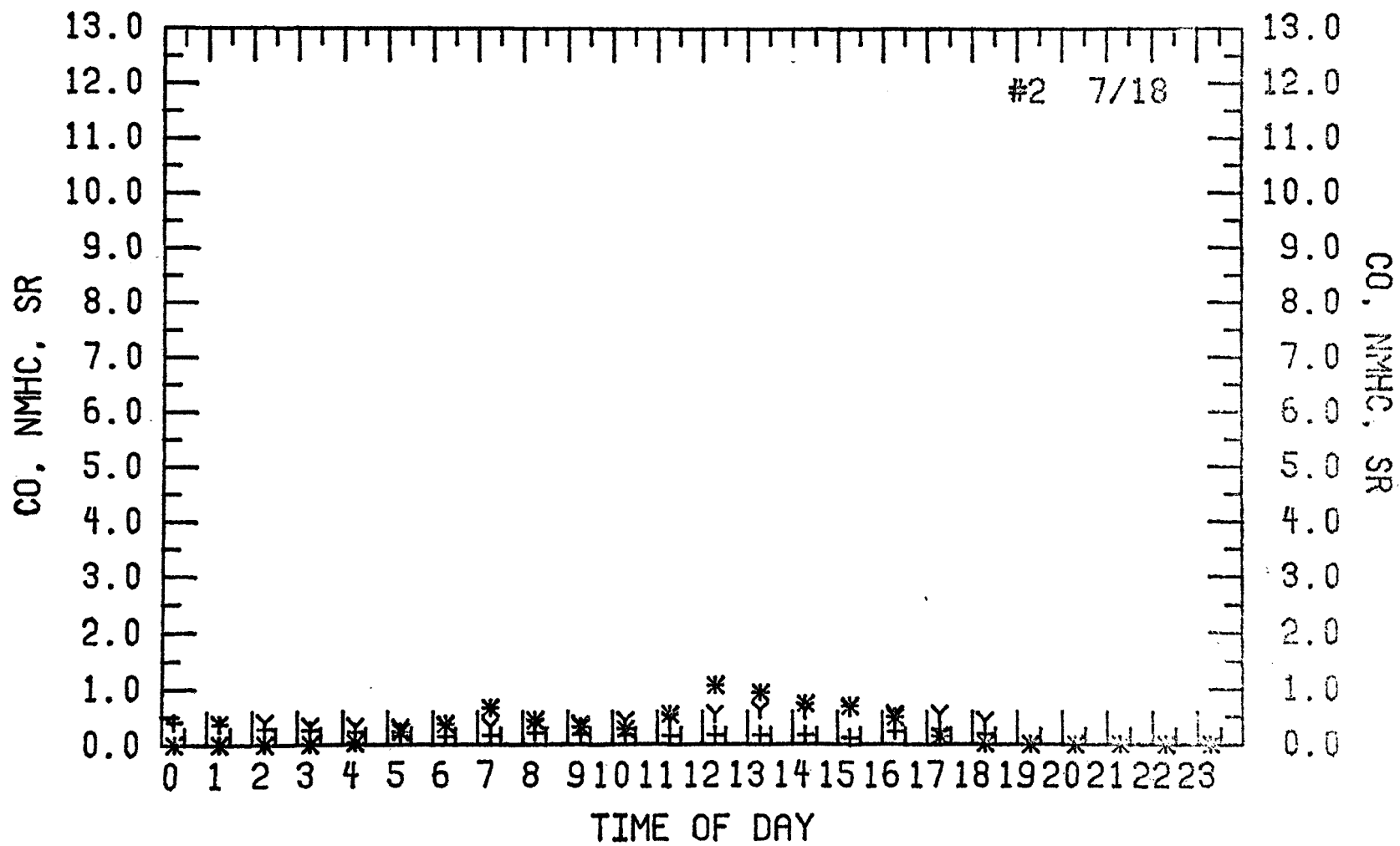


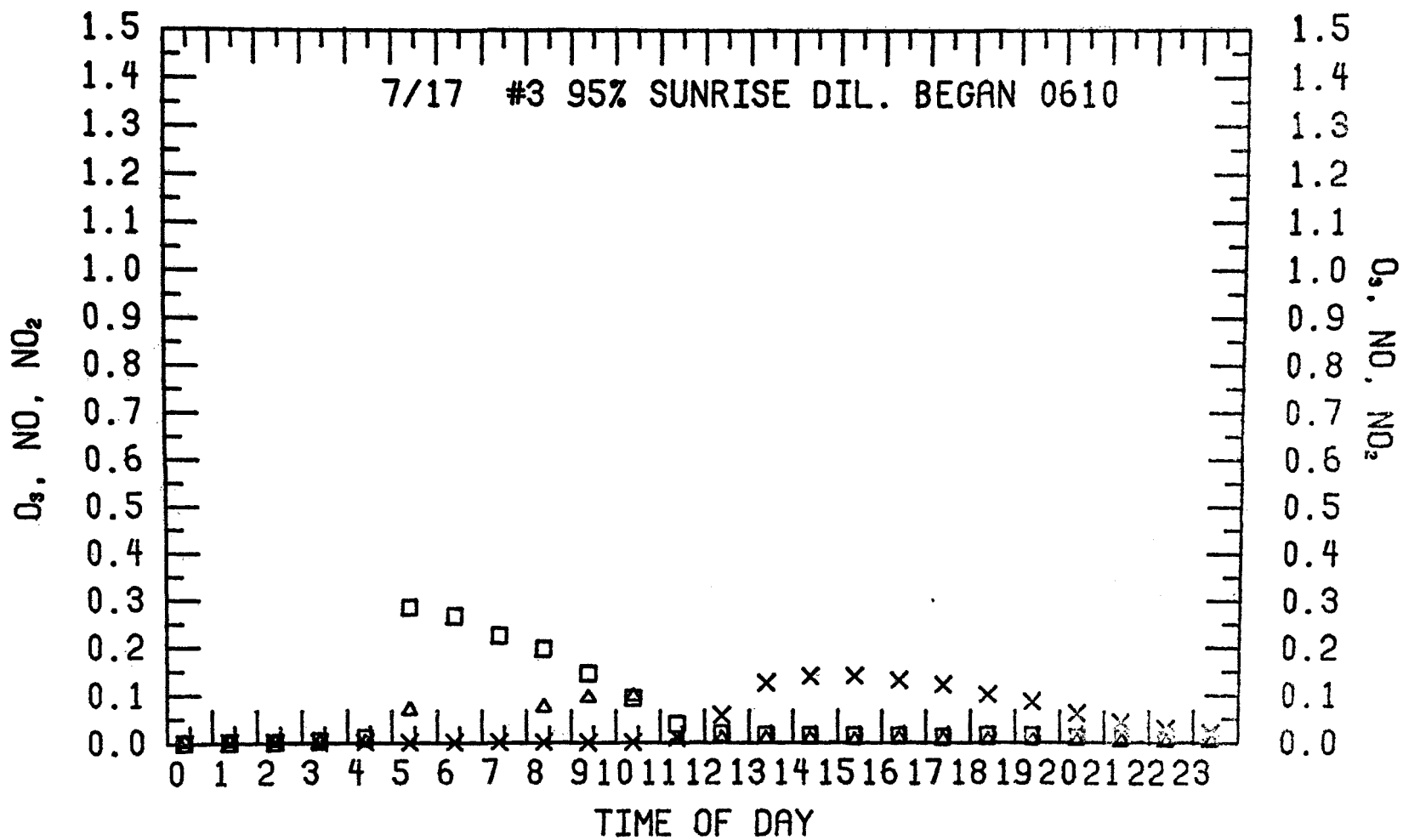




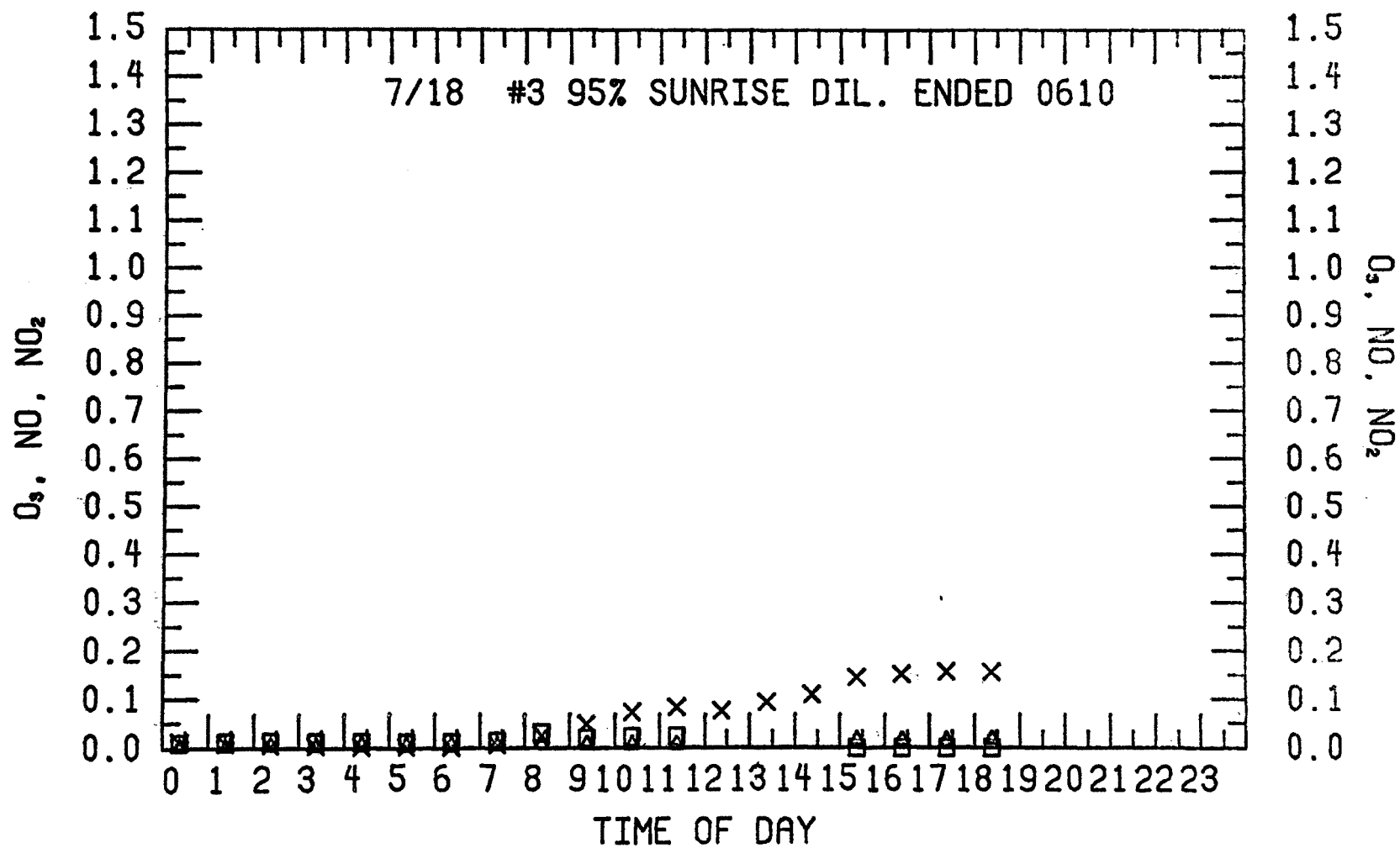


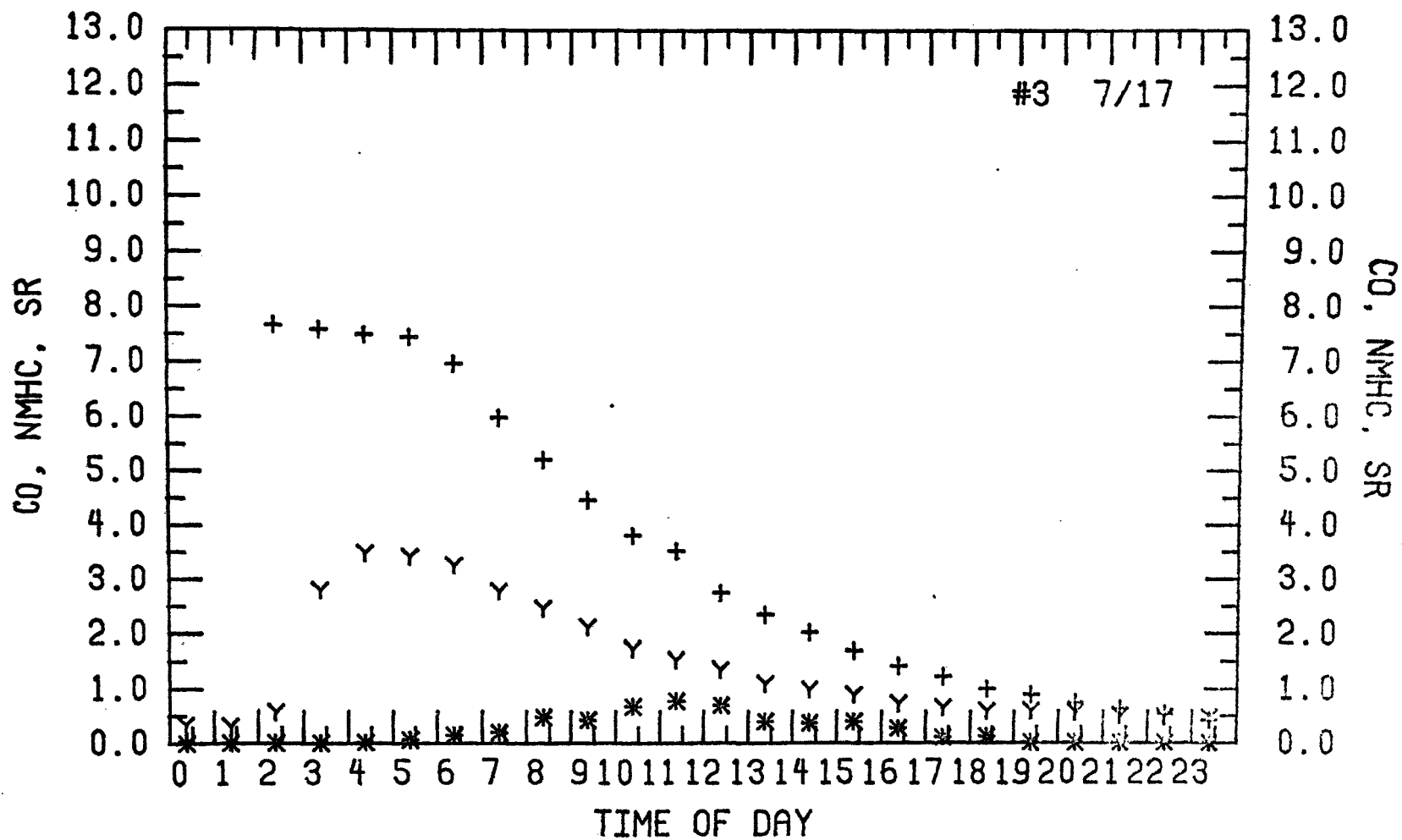


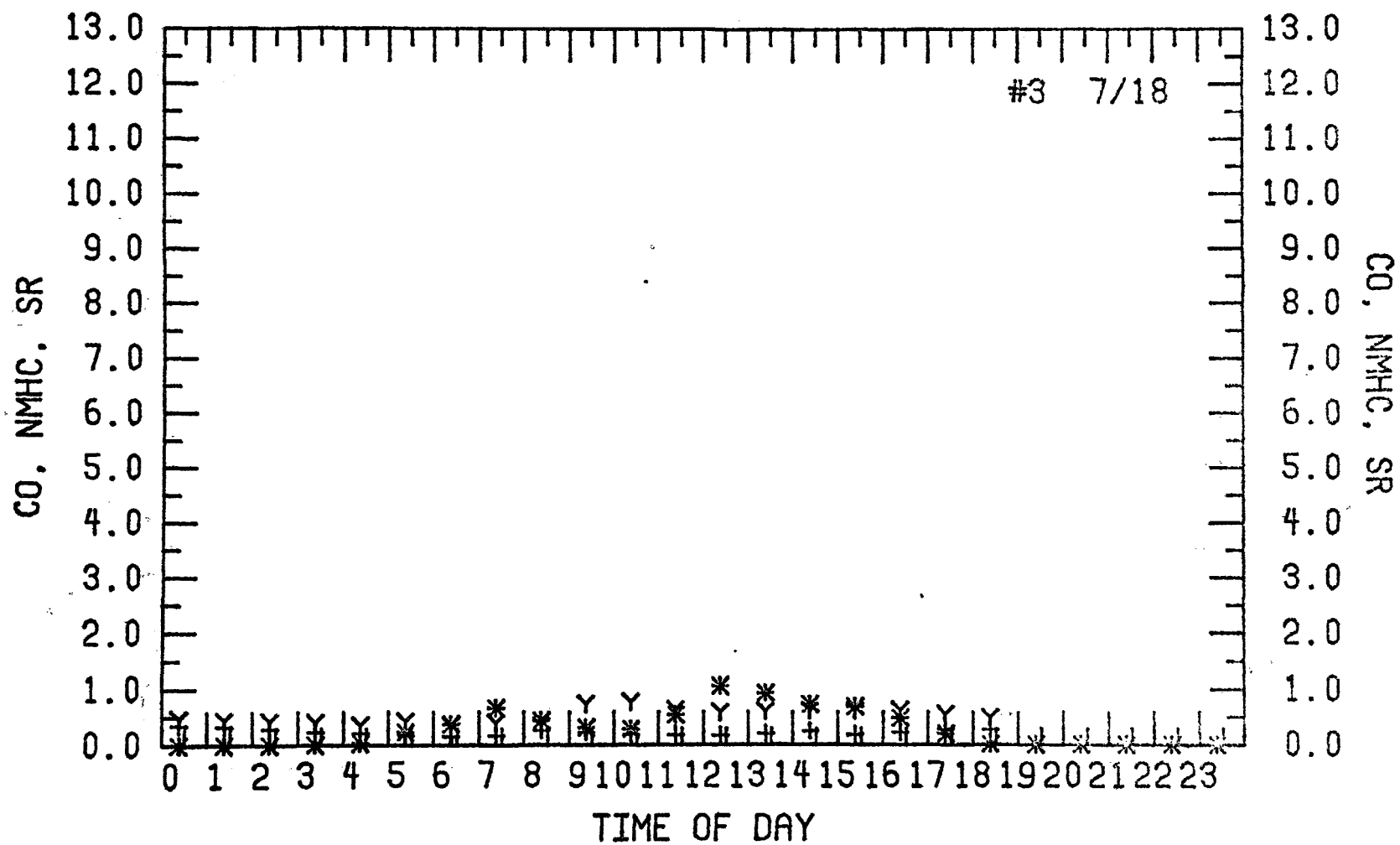


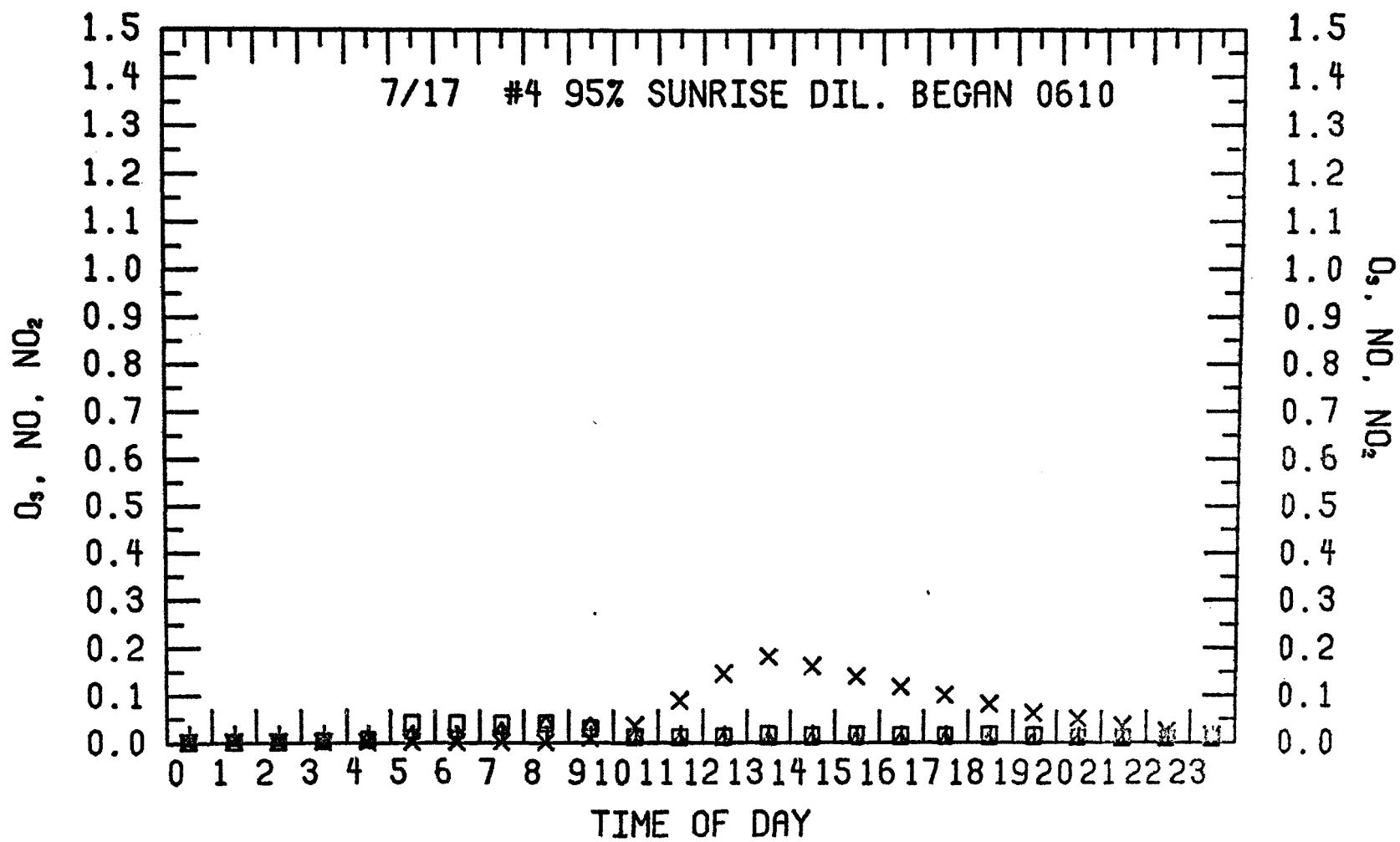


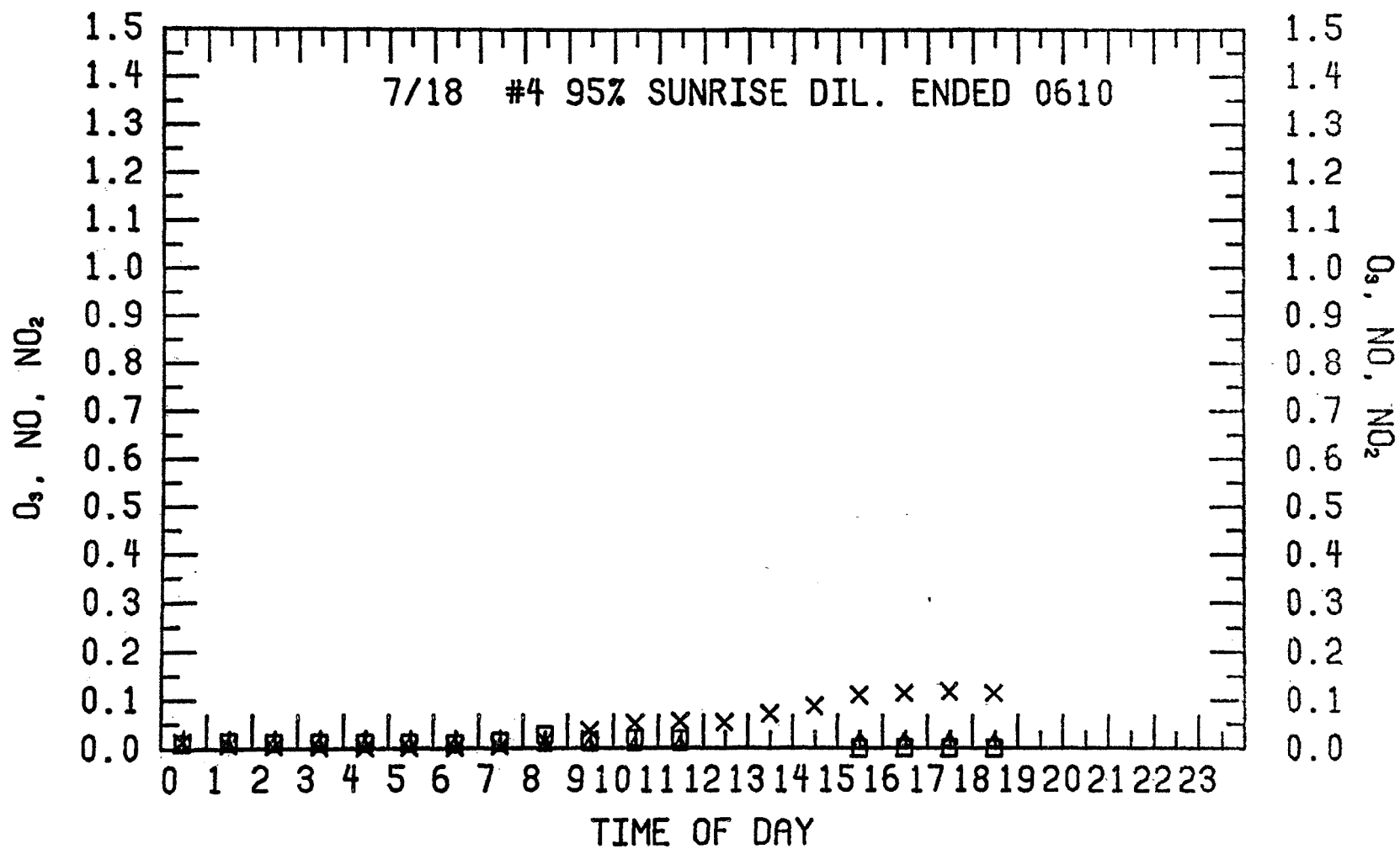


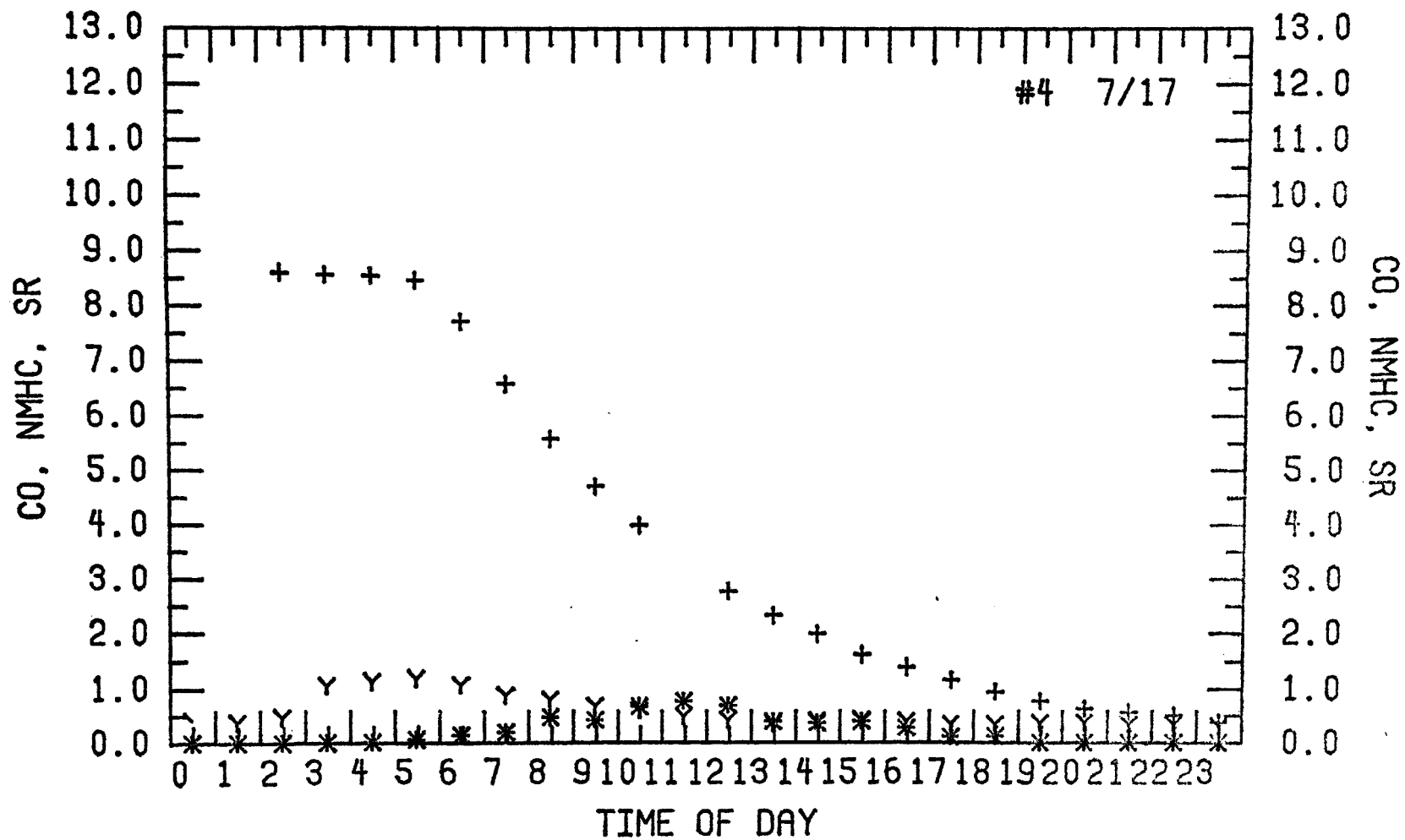


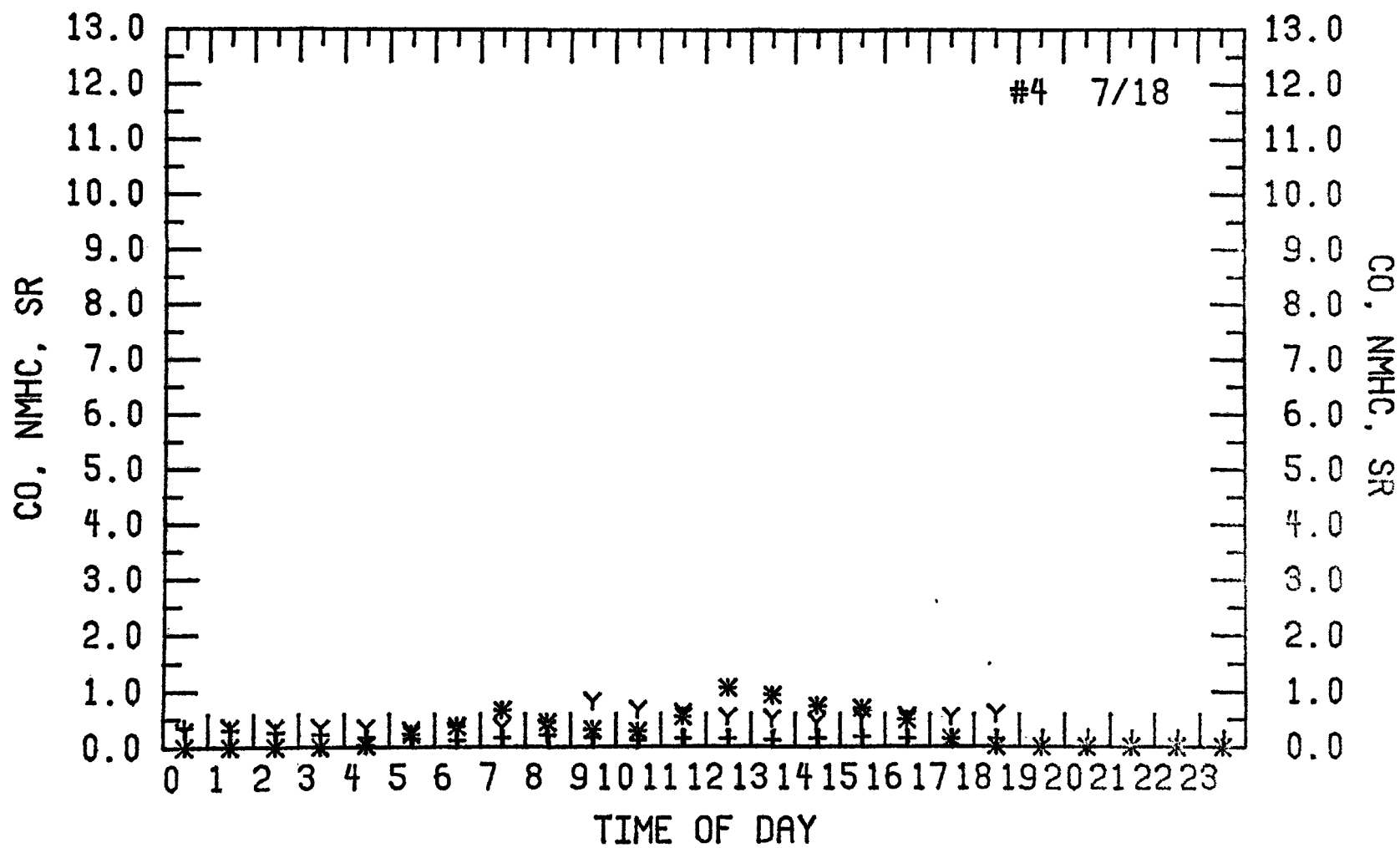


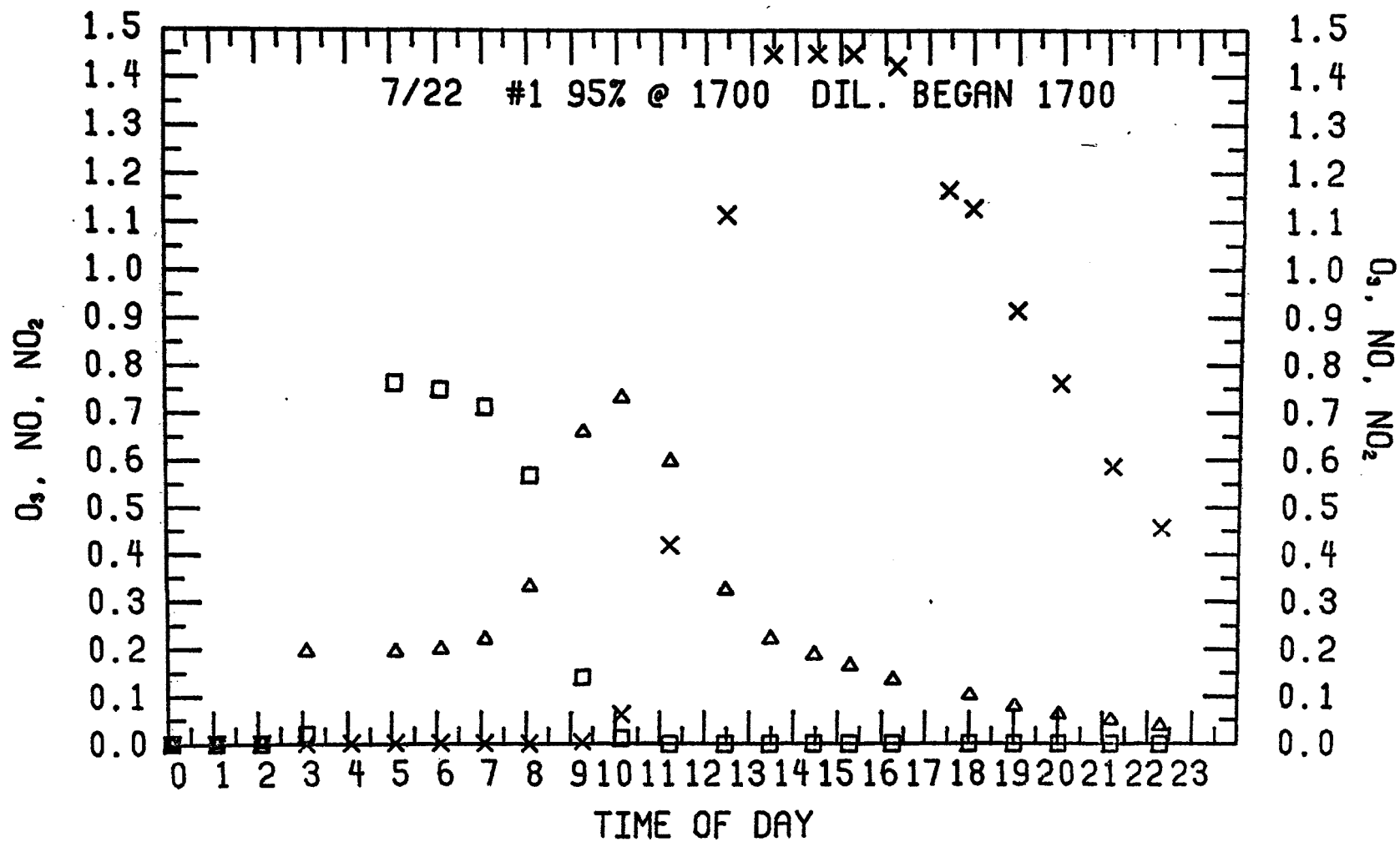




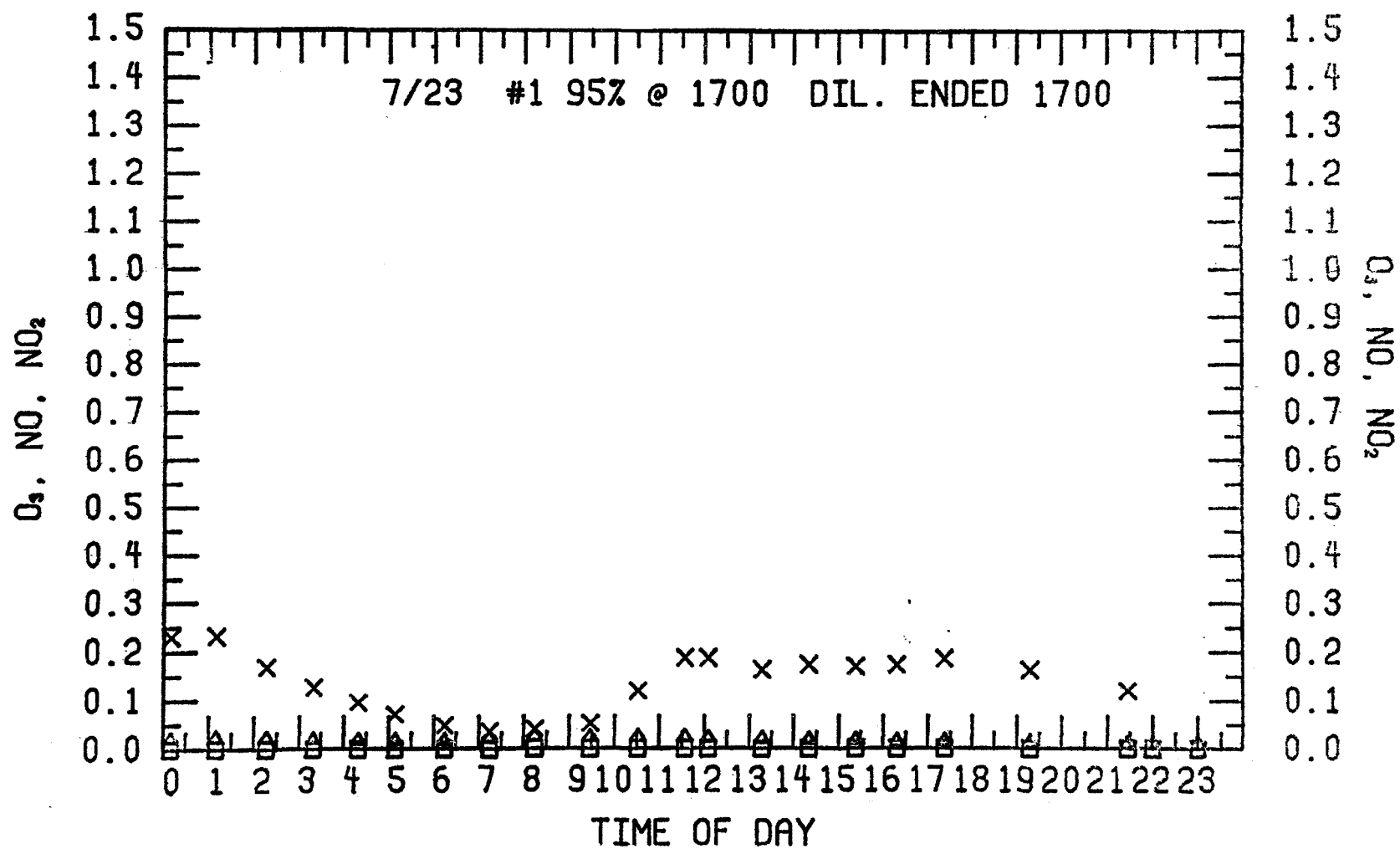


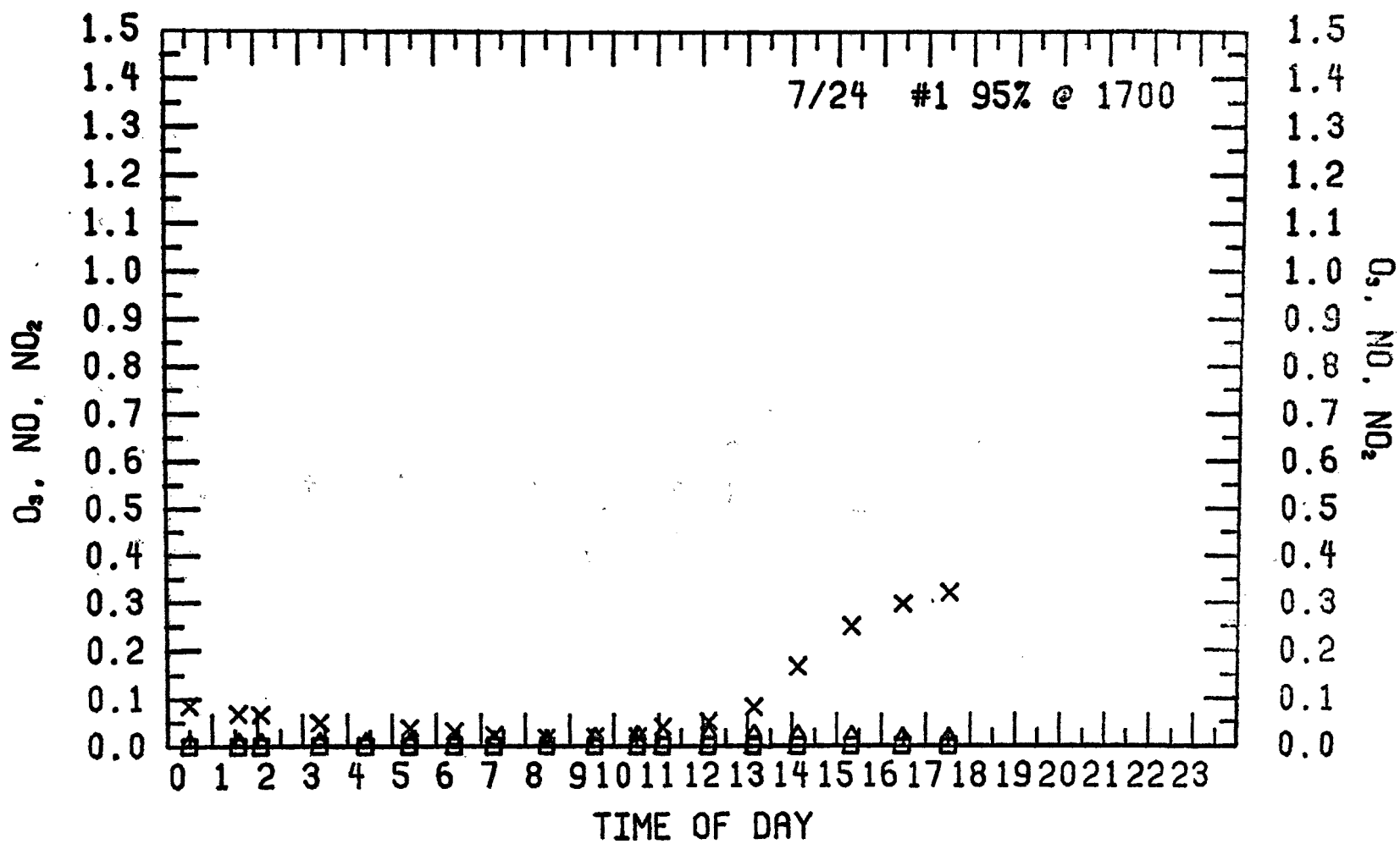


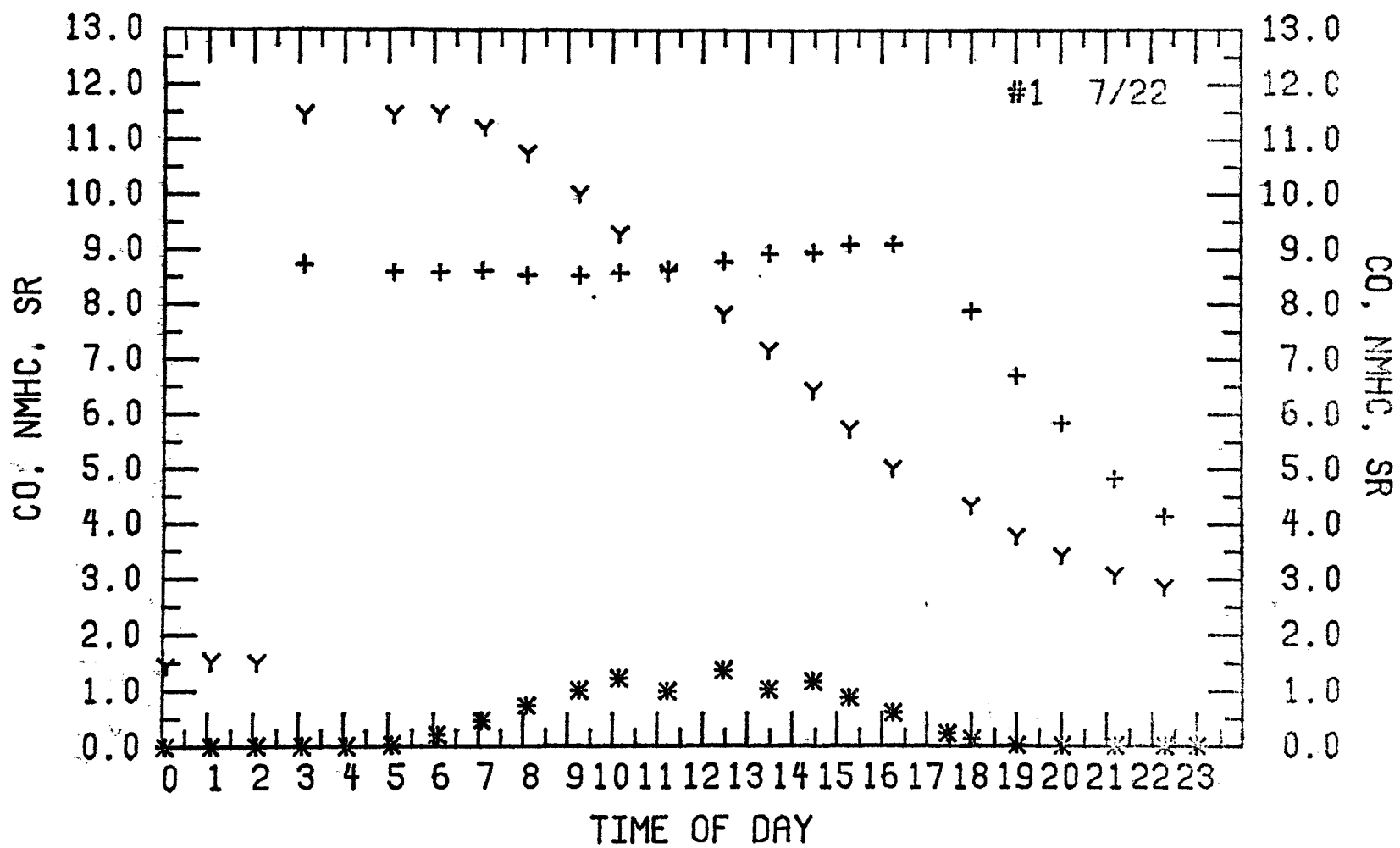


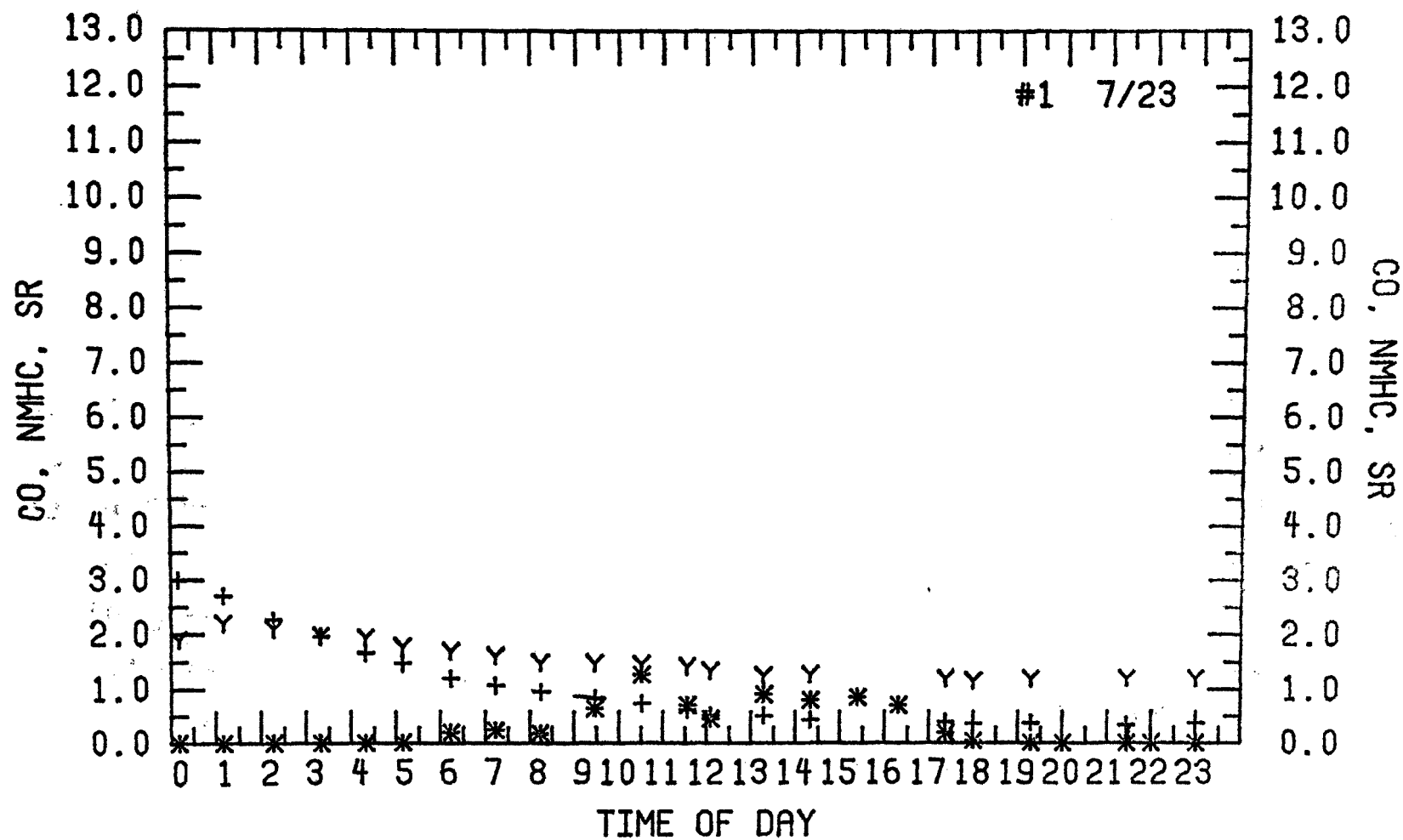




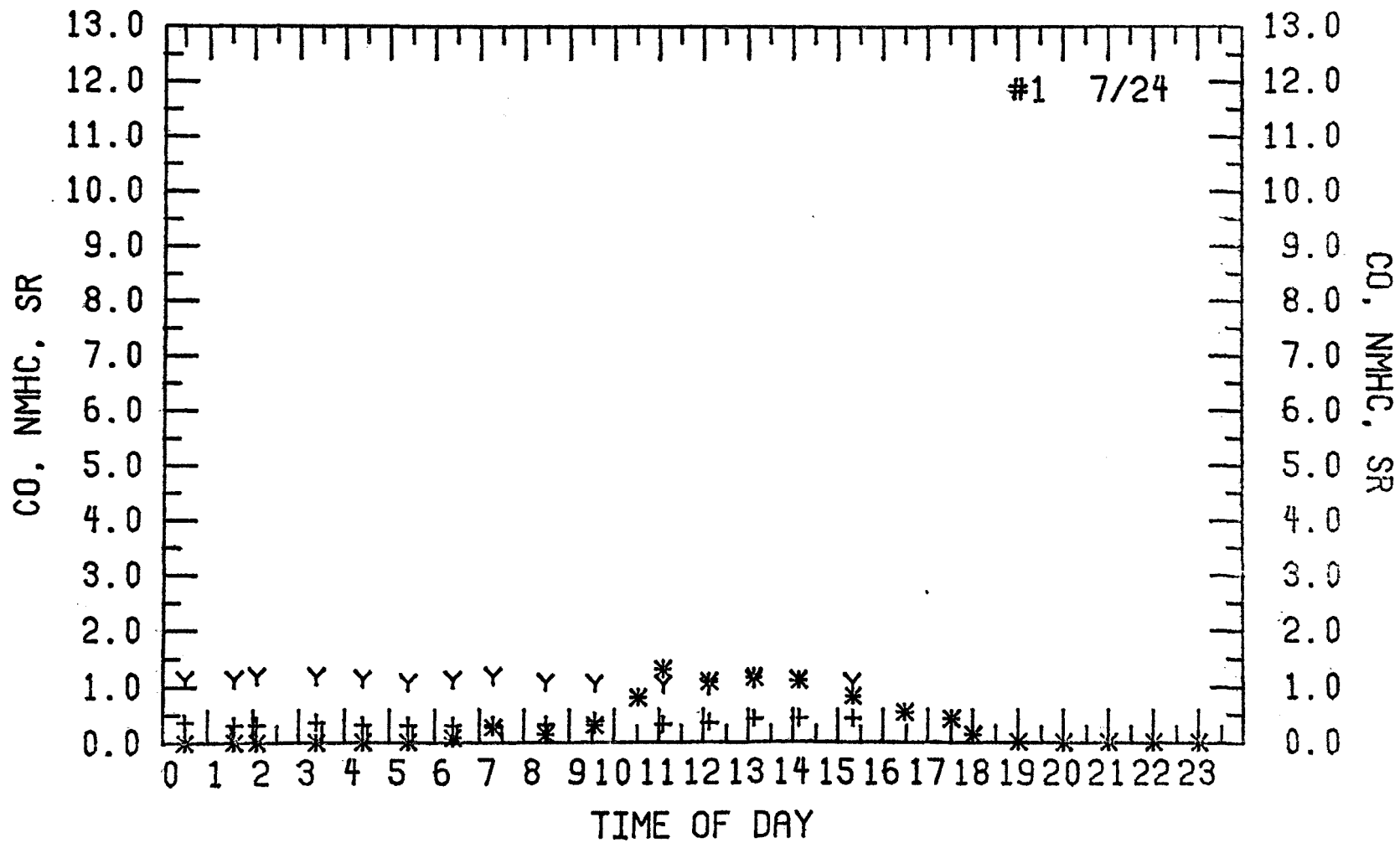


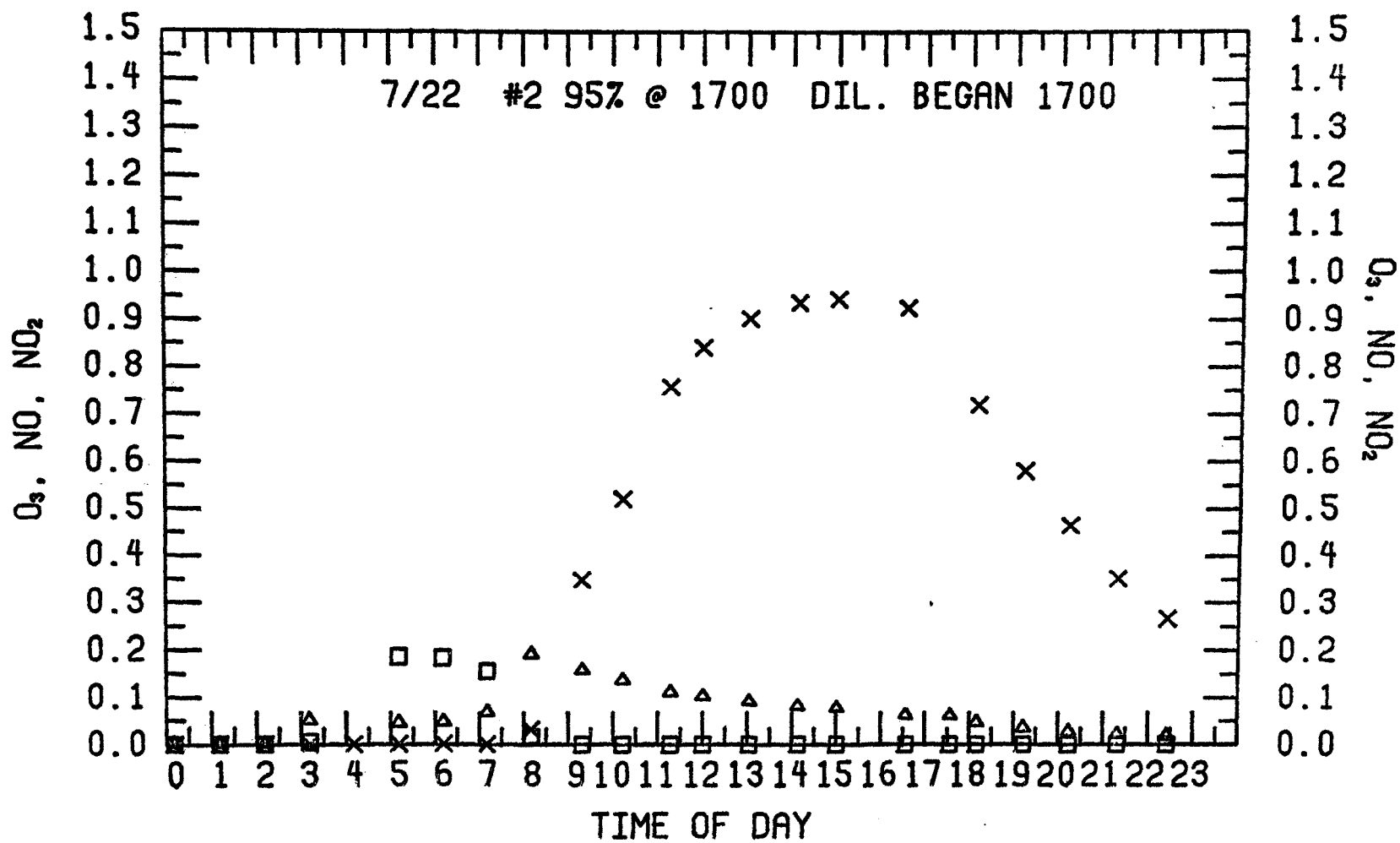


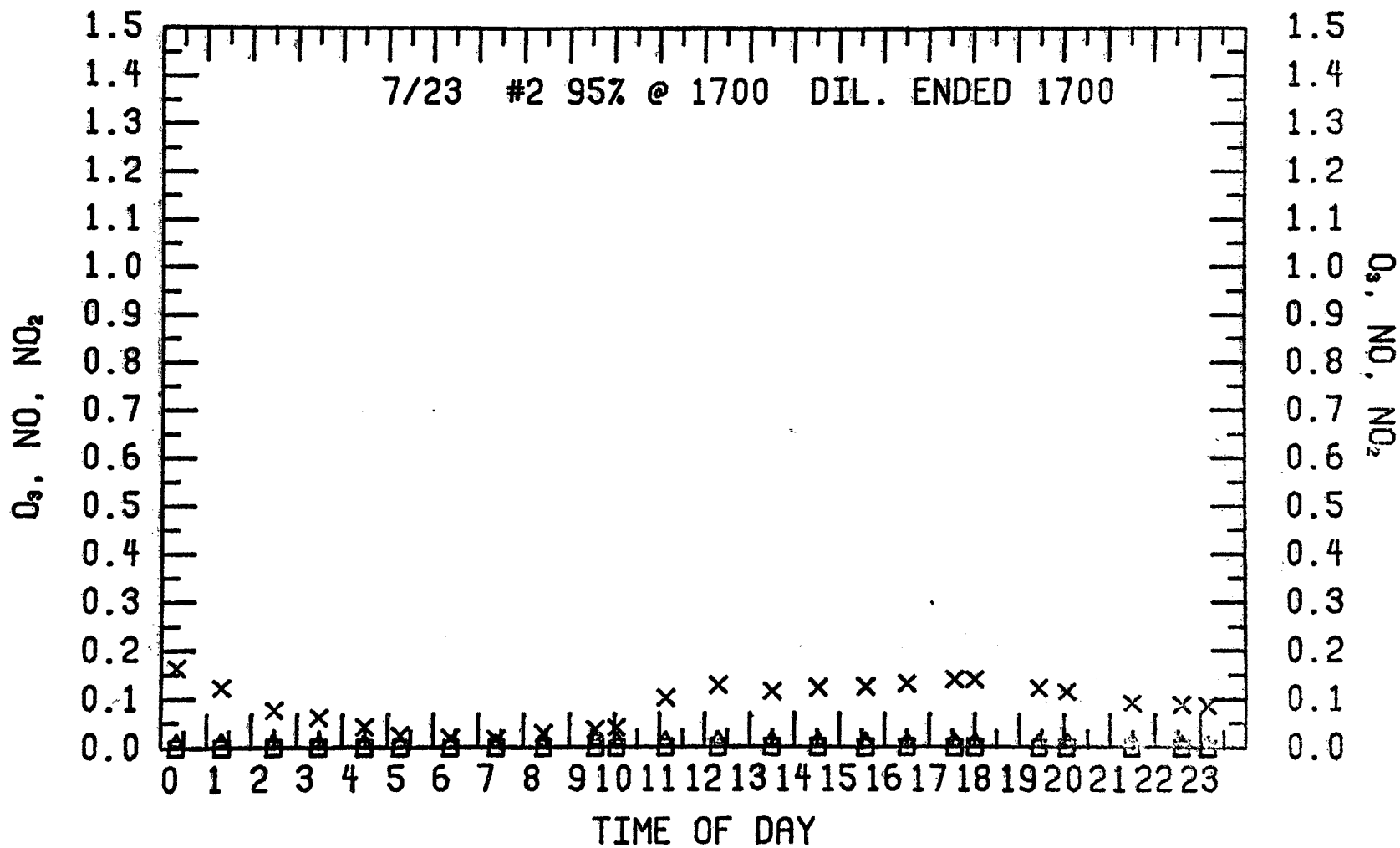


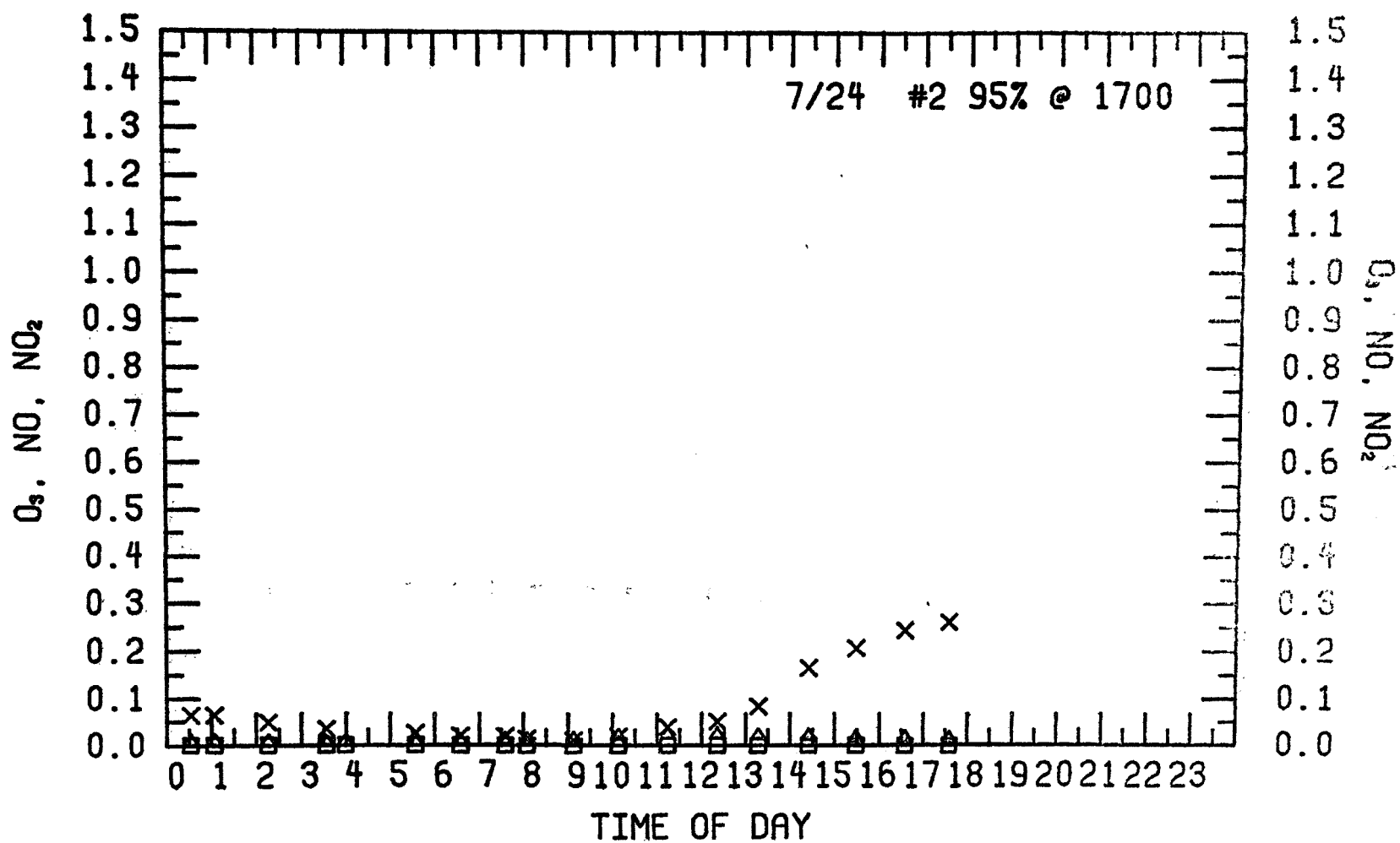


100

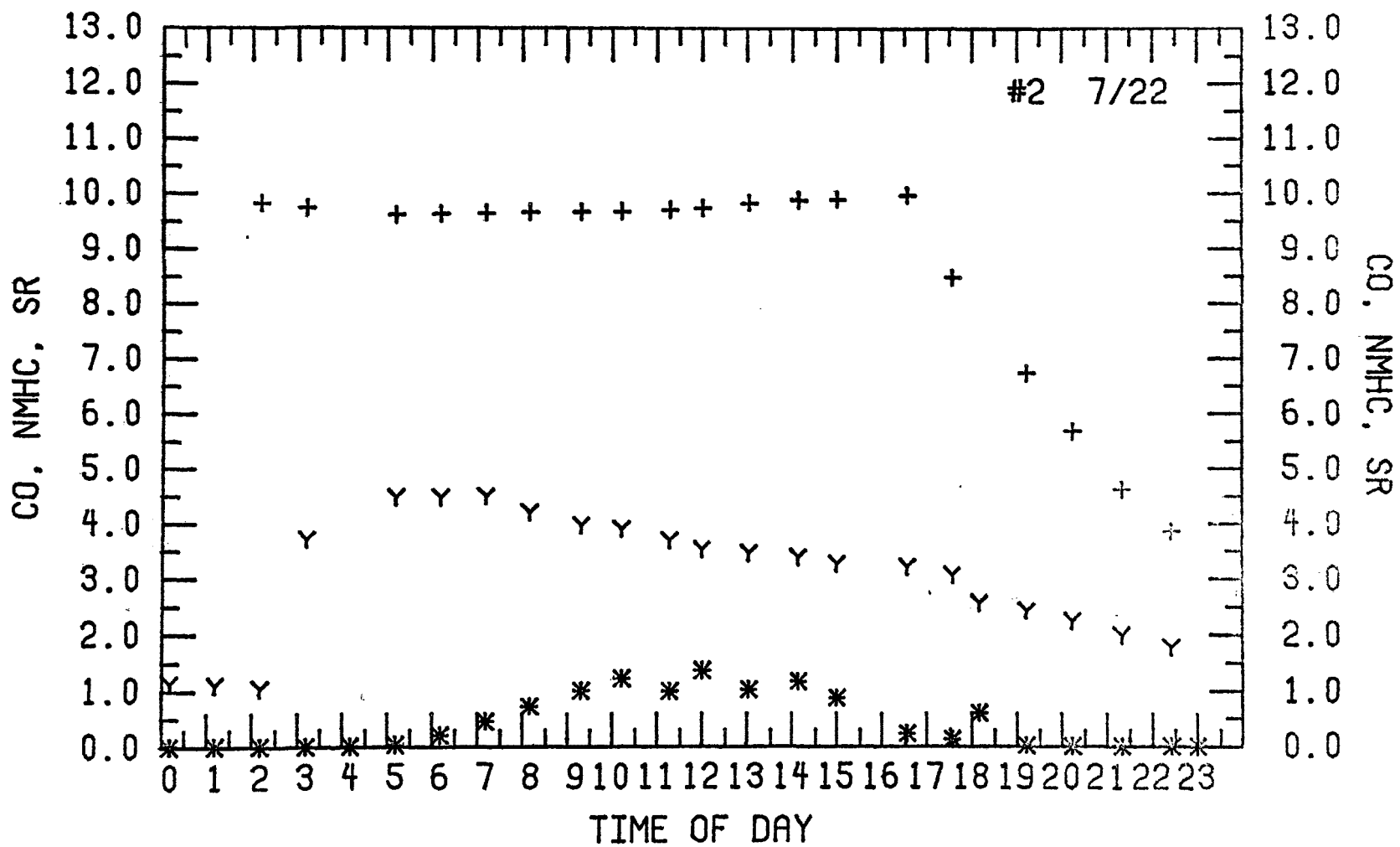


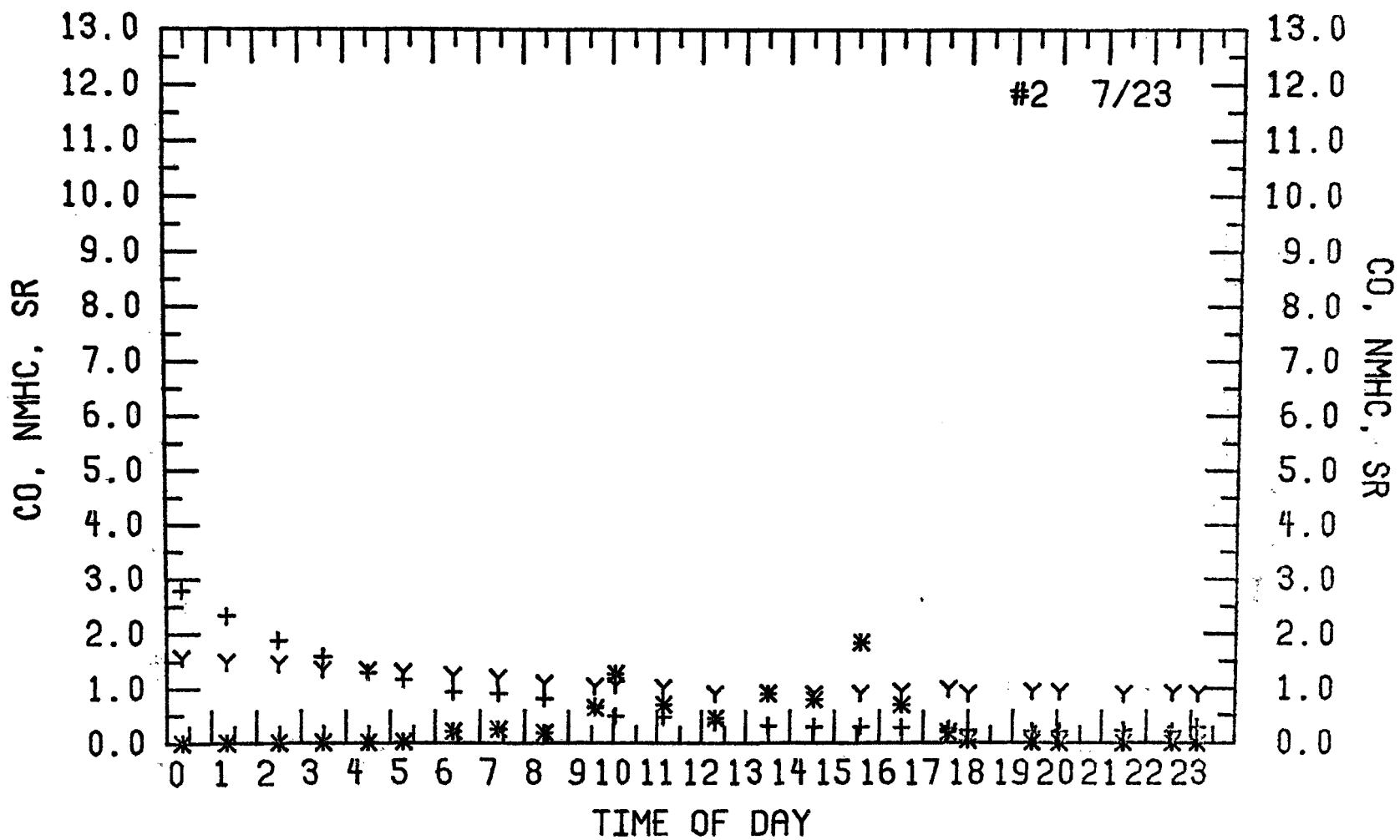


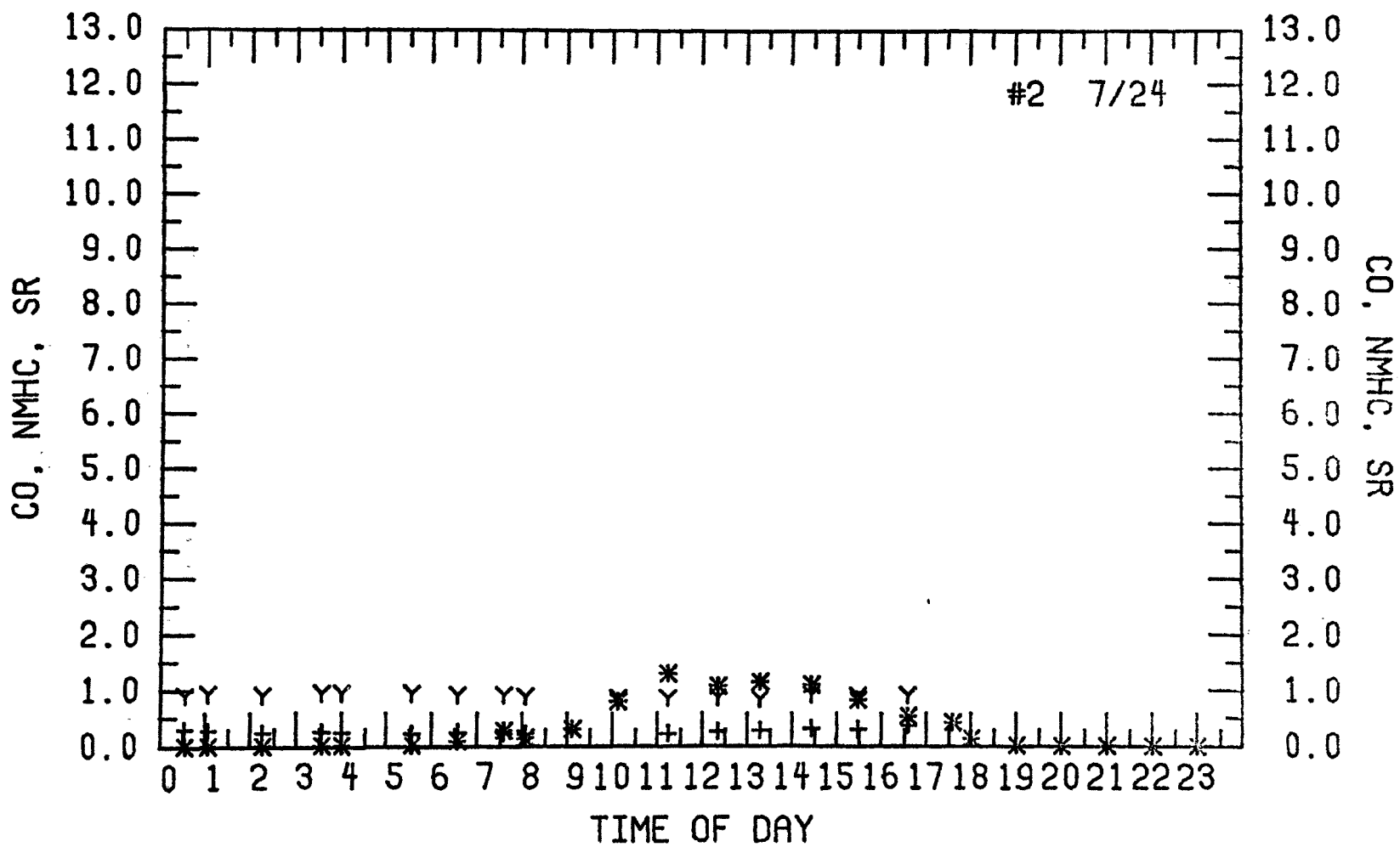


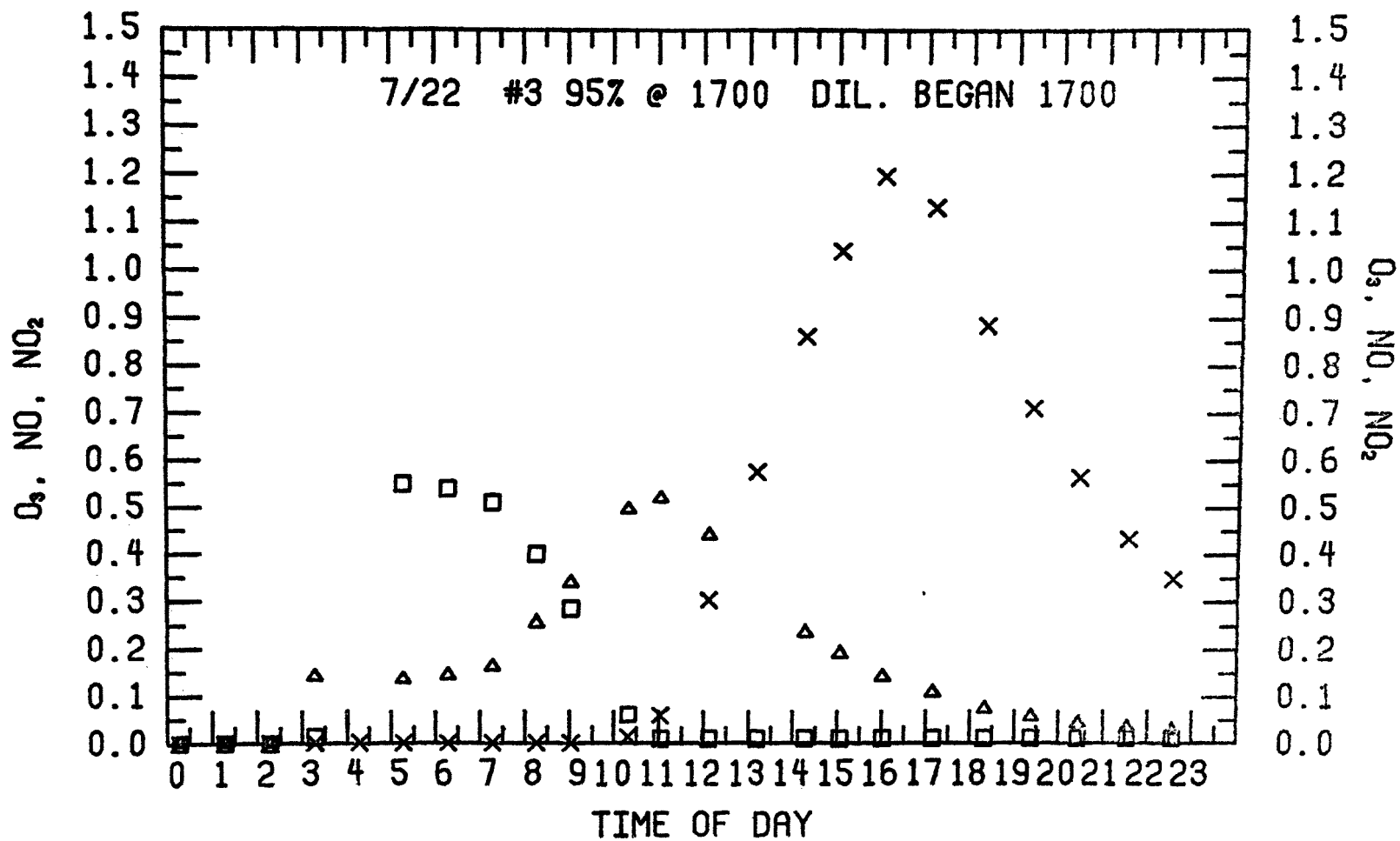


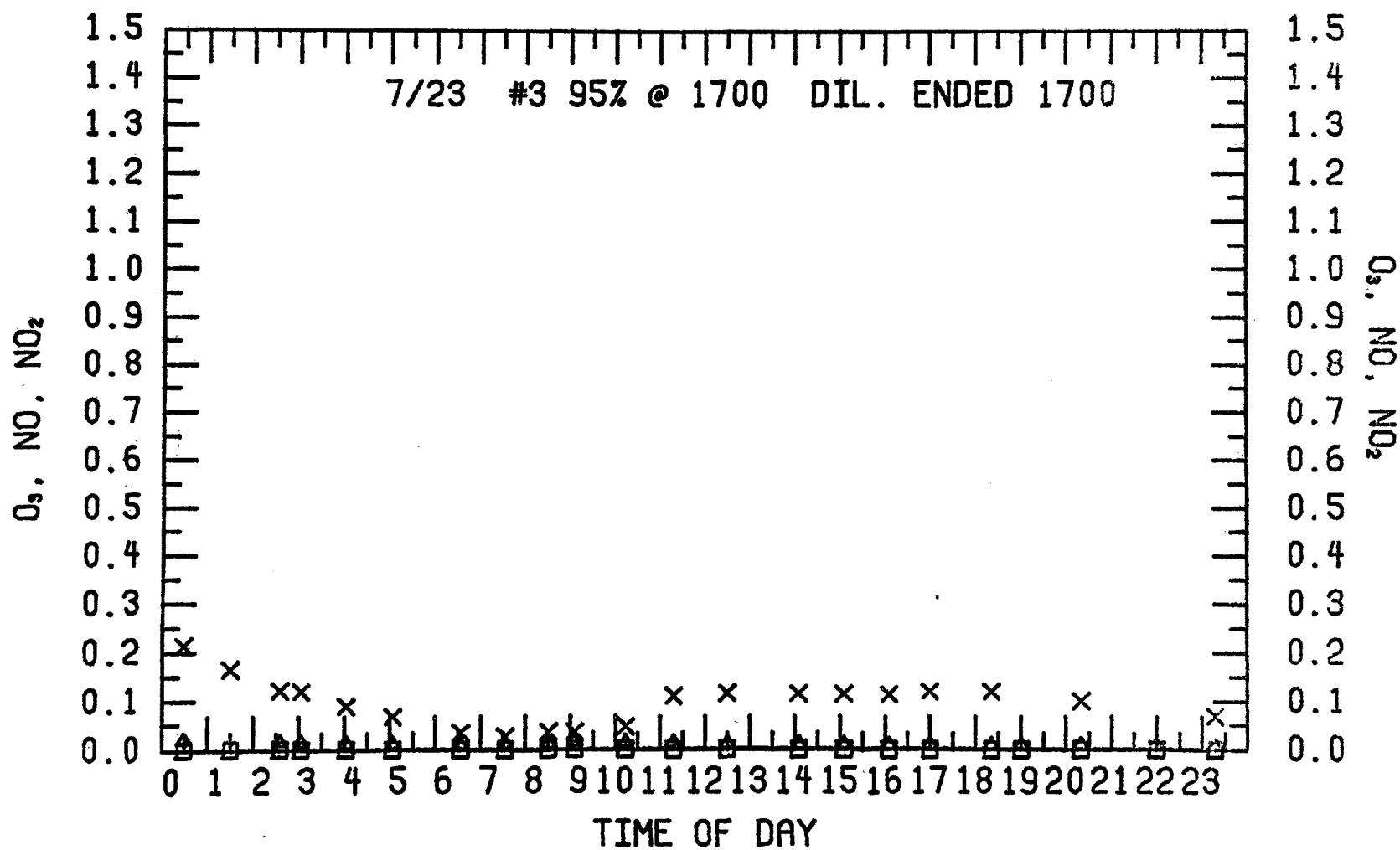


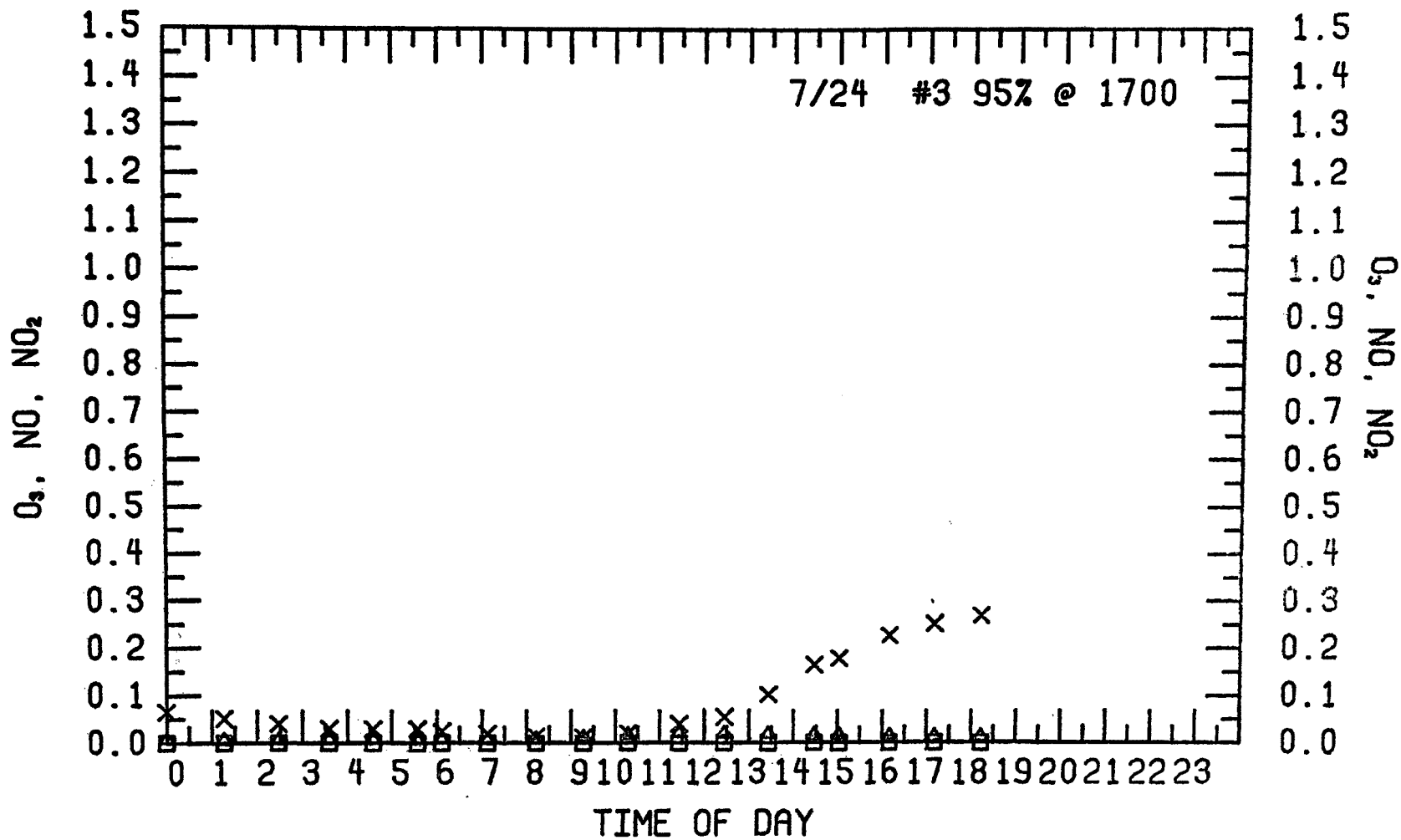


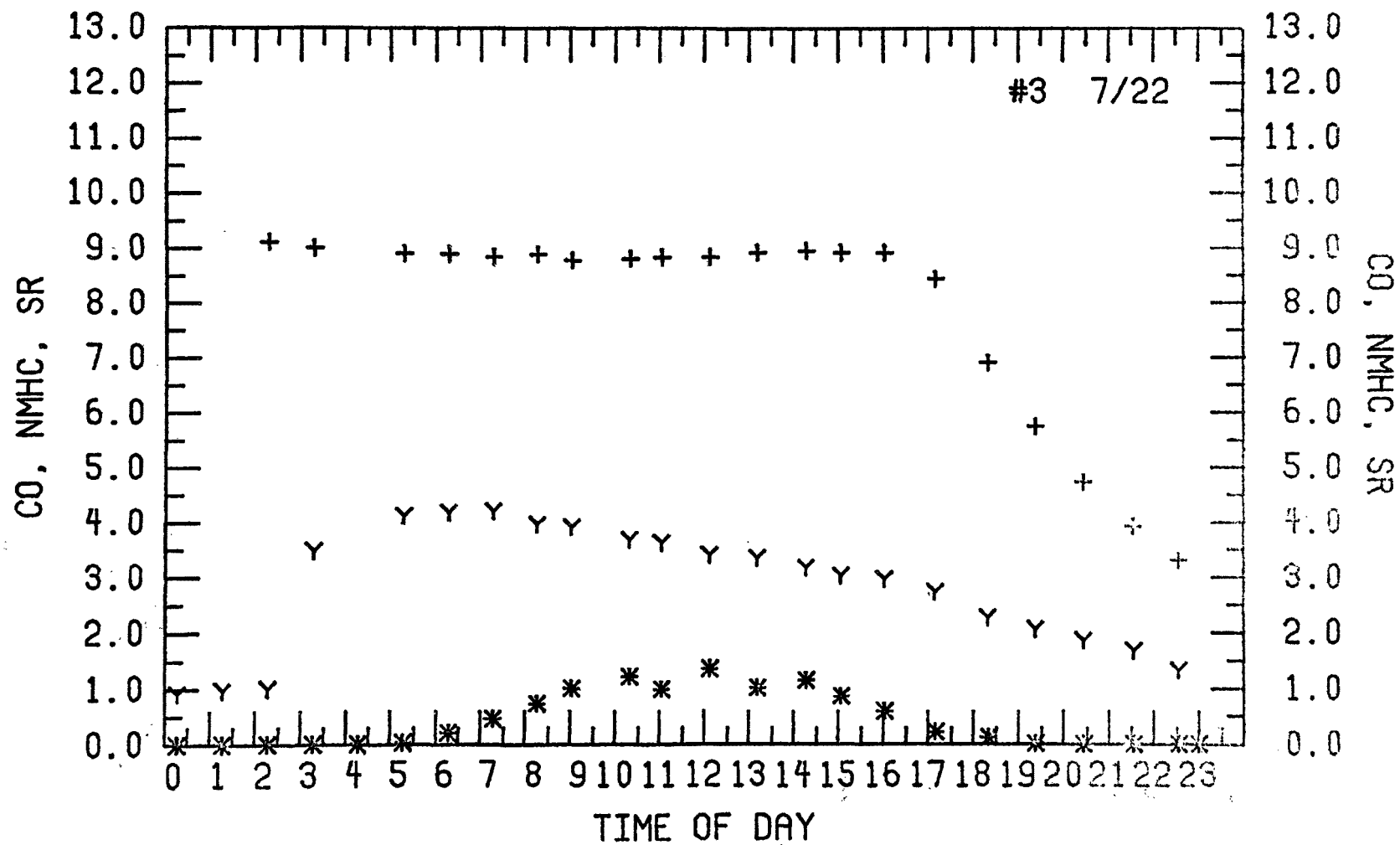


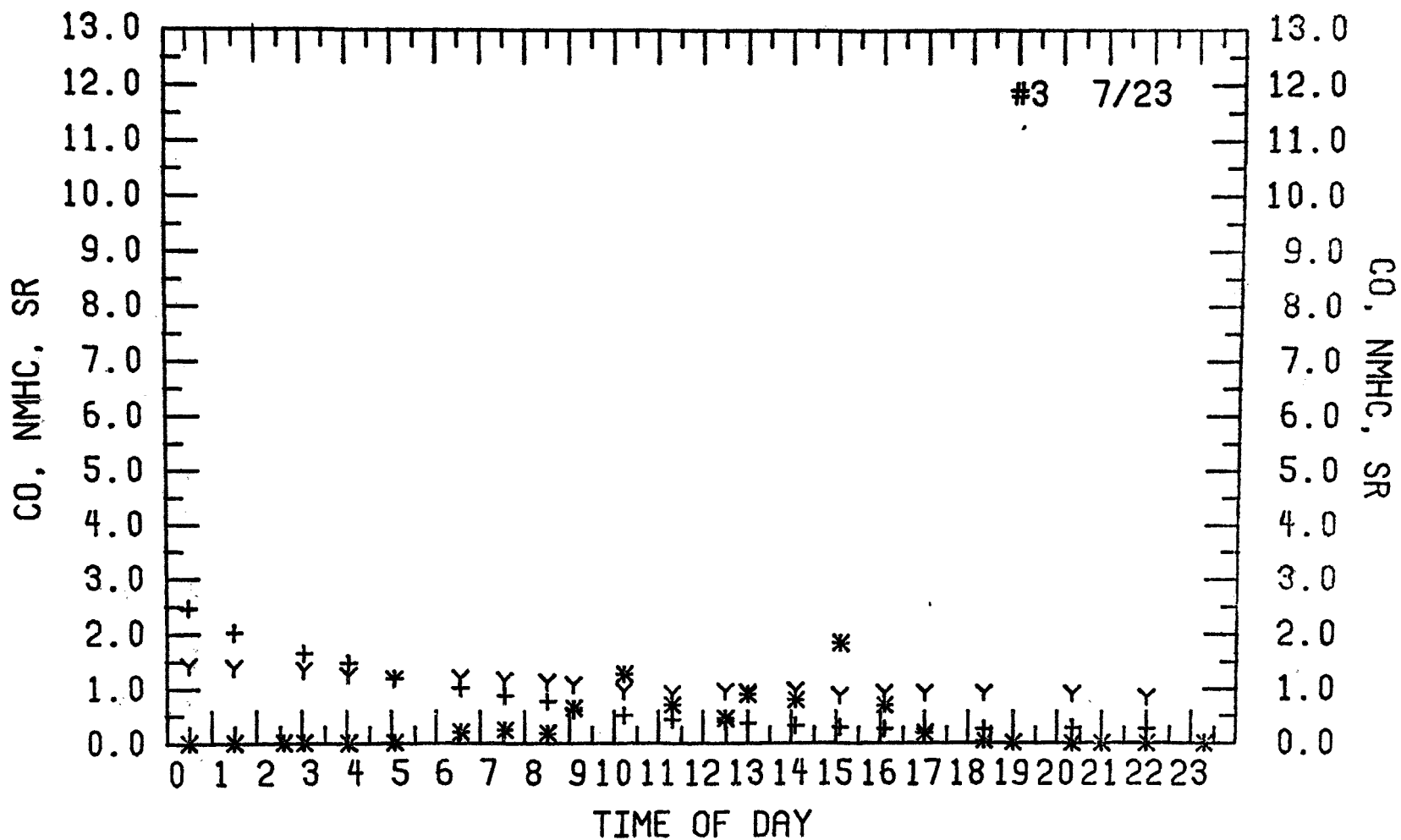




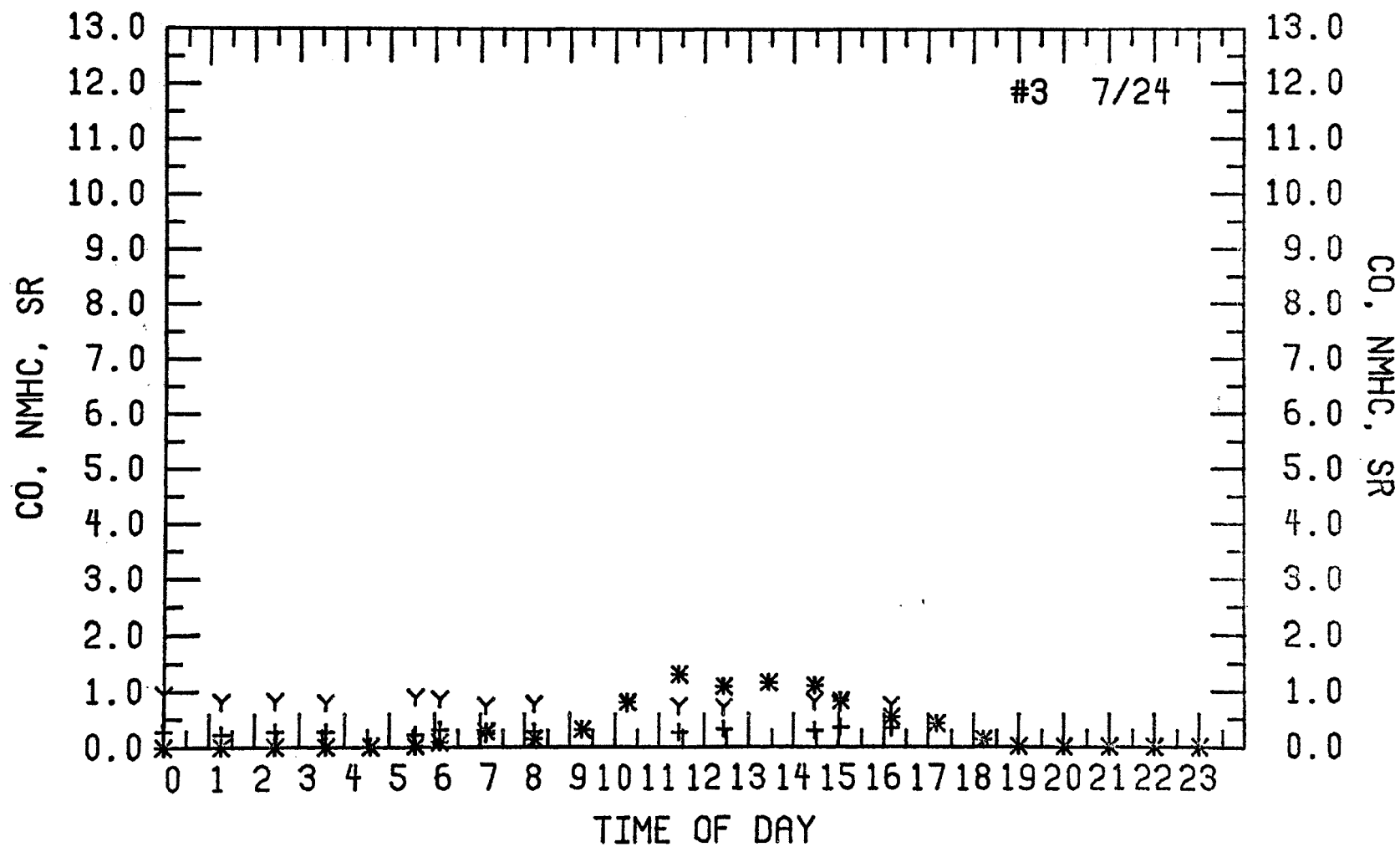


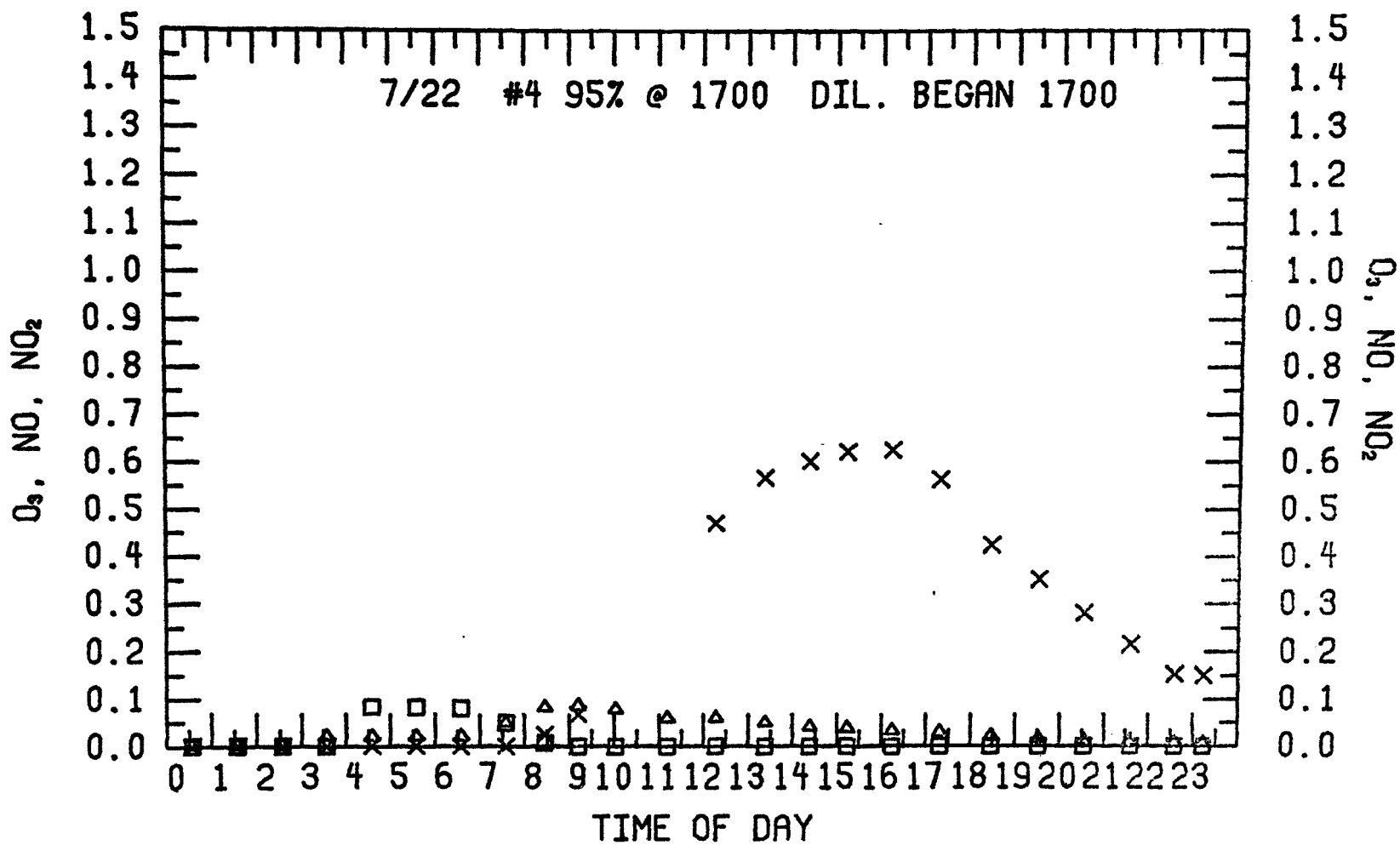


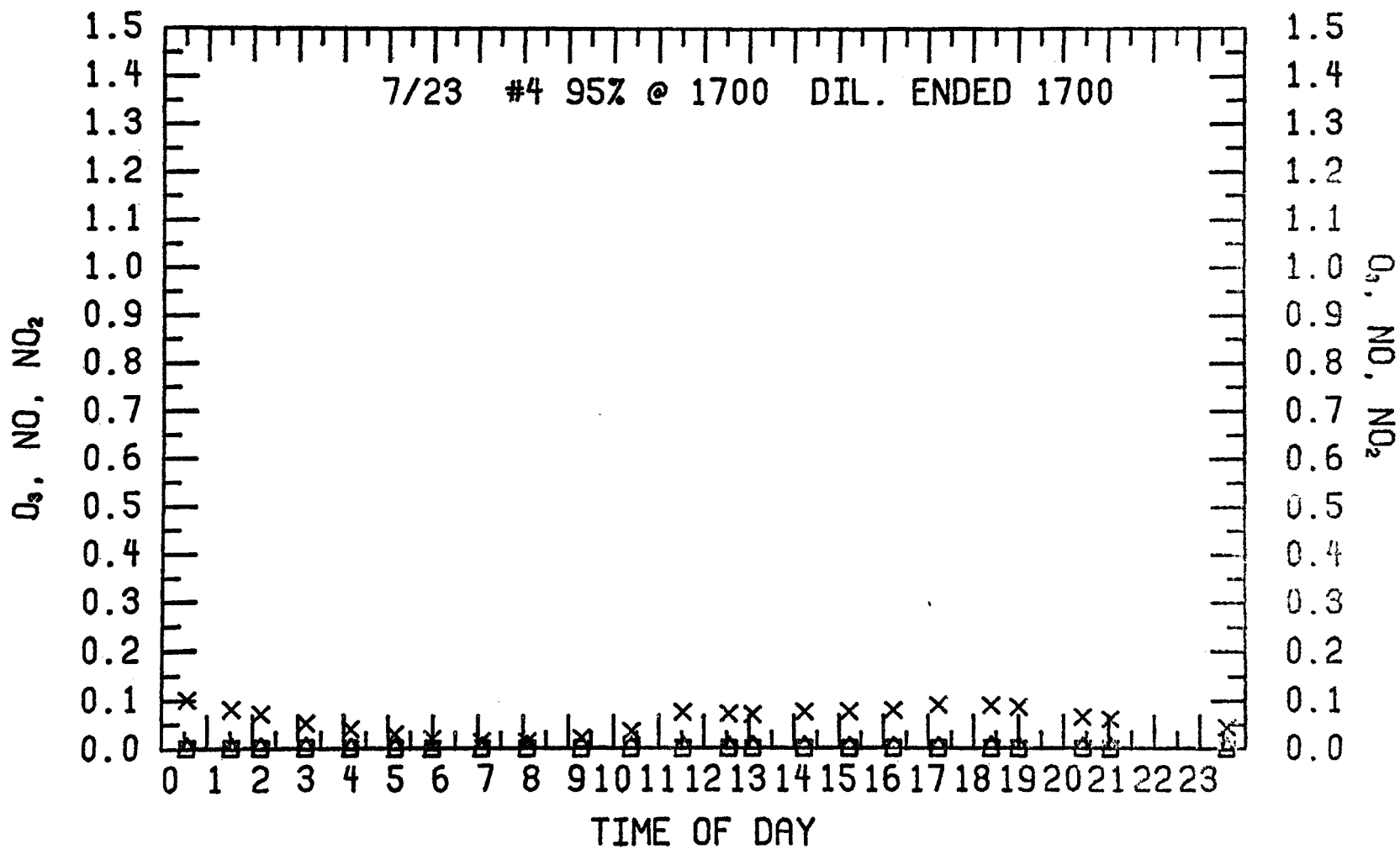


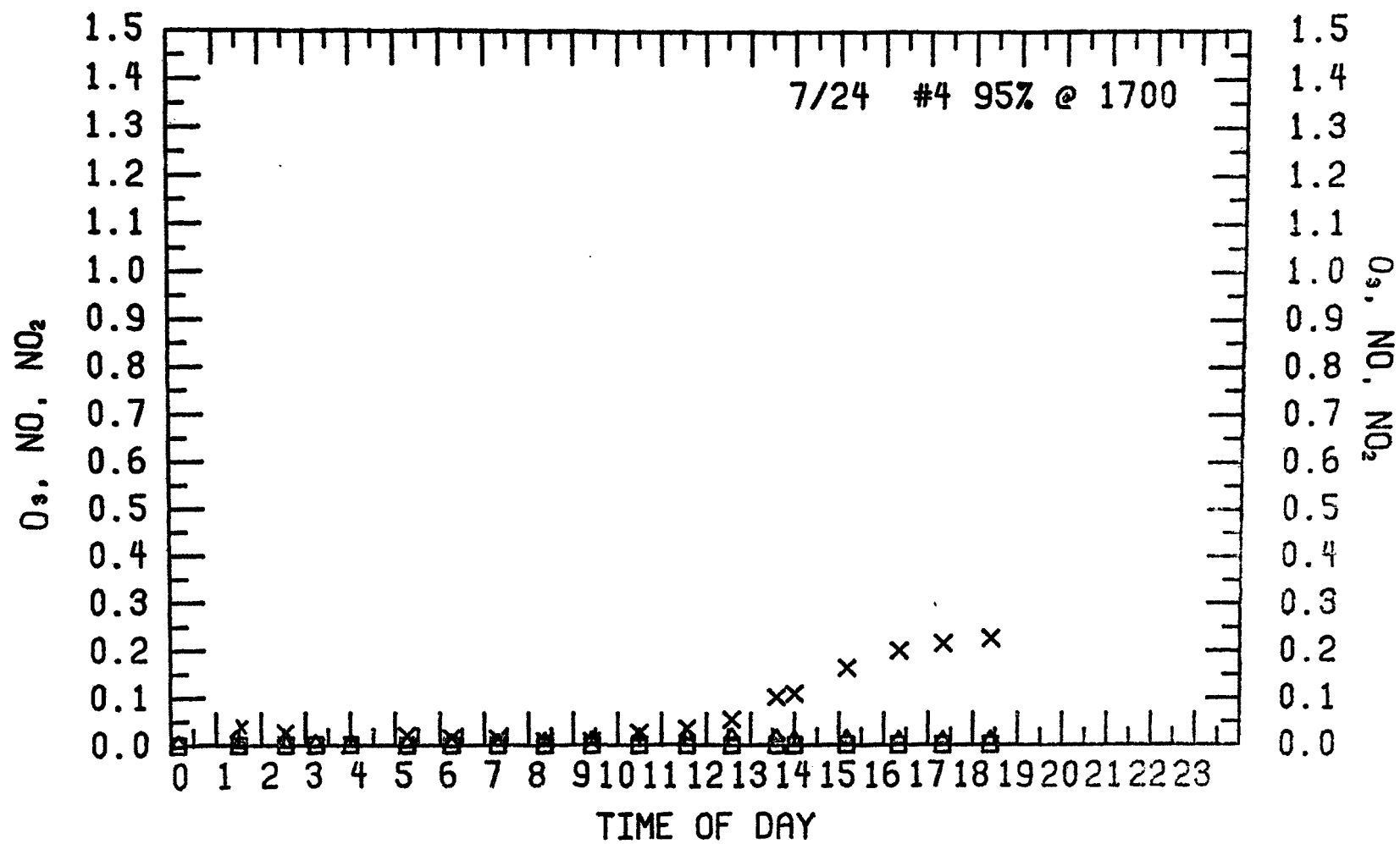


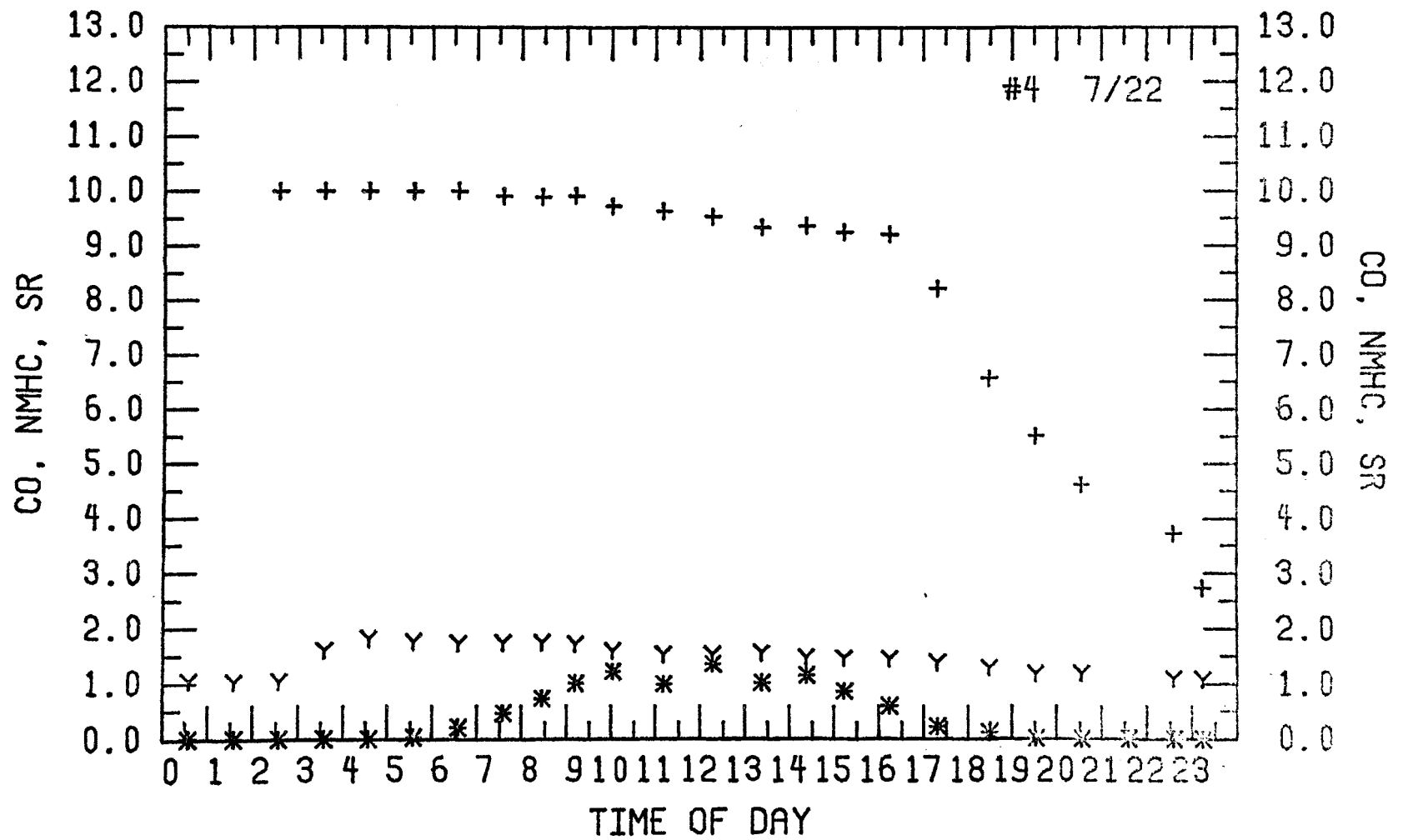


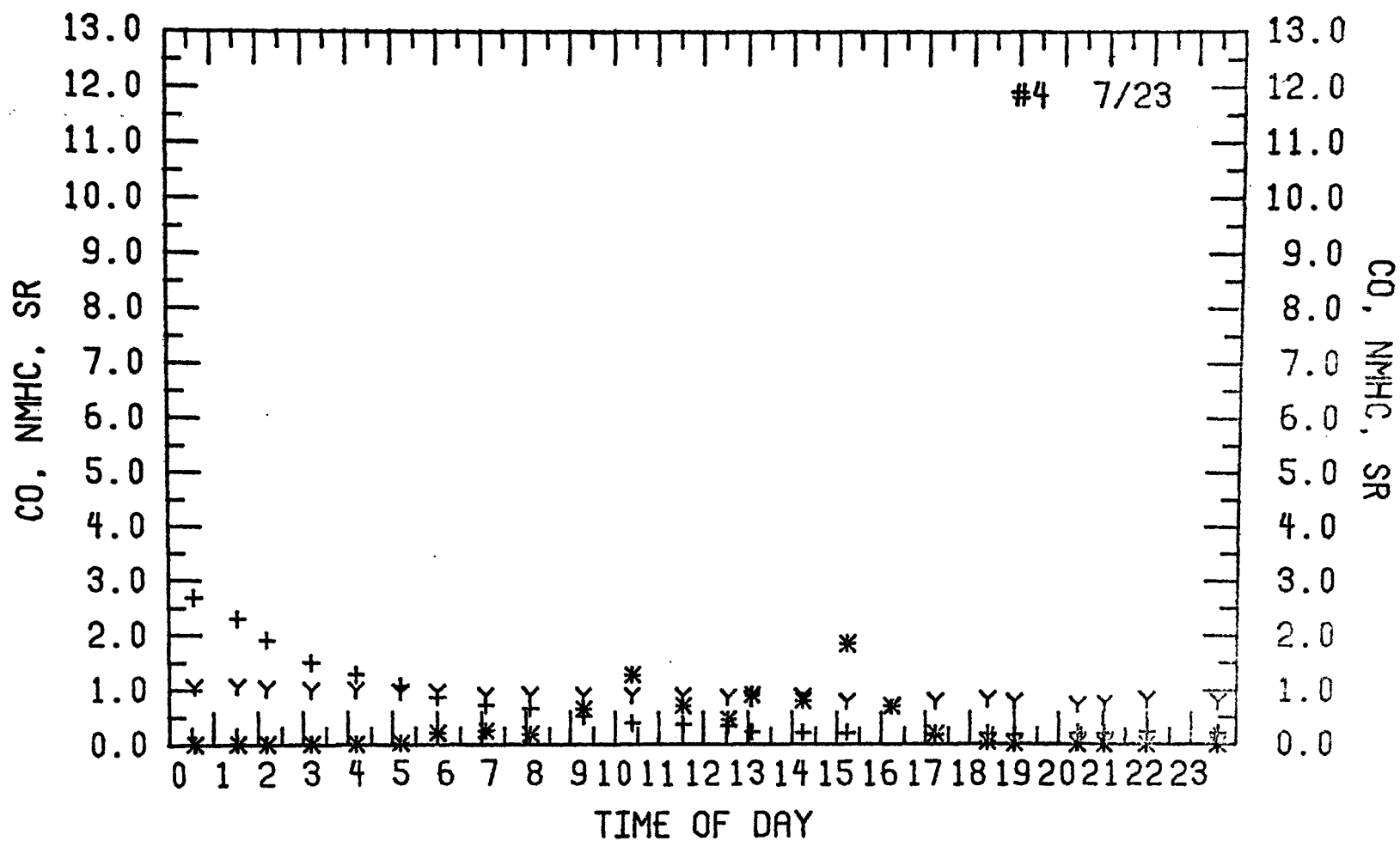


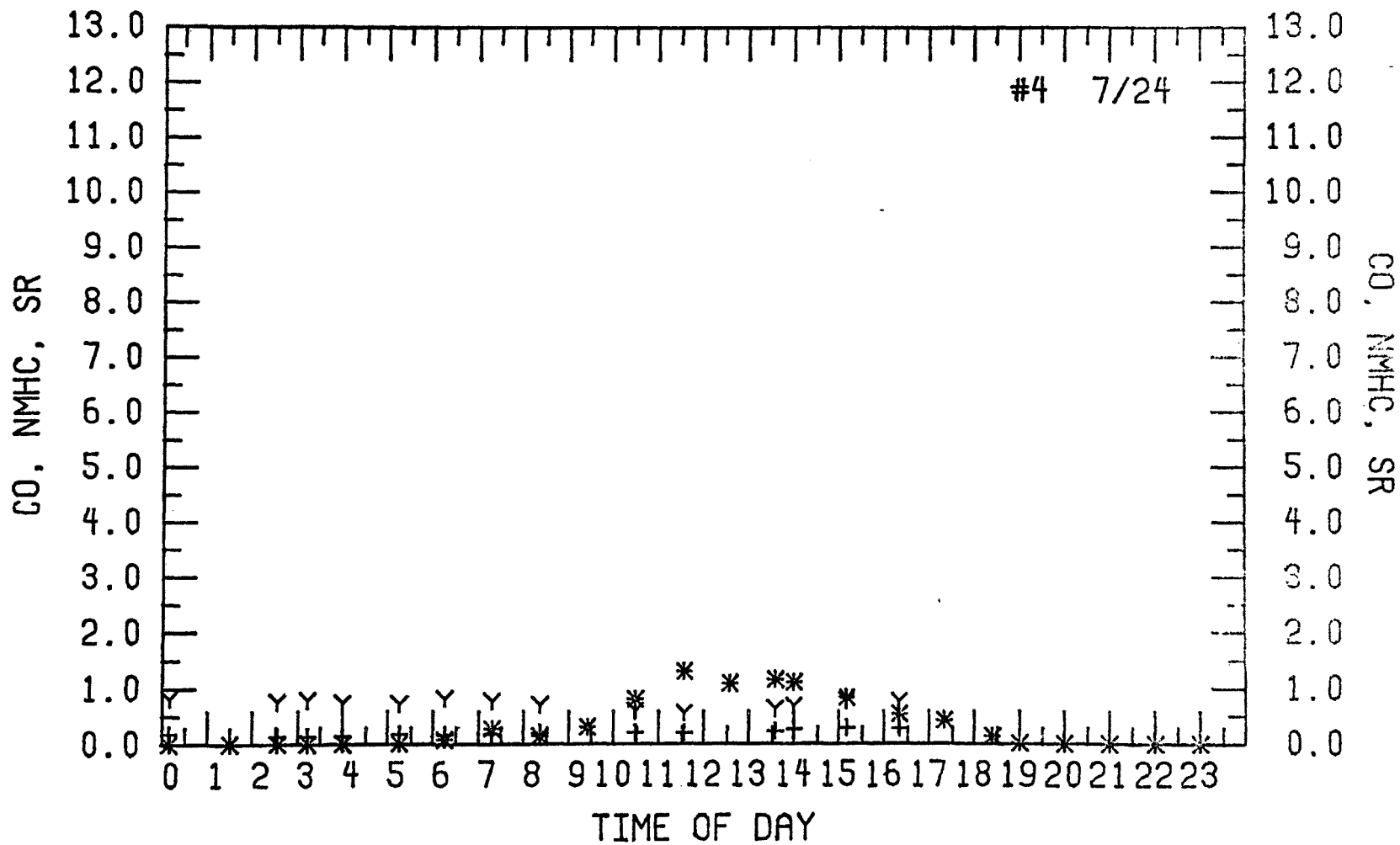


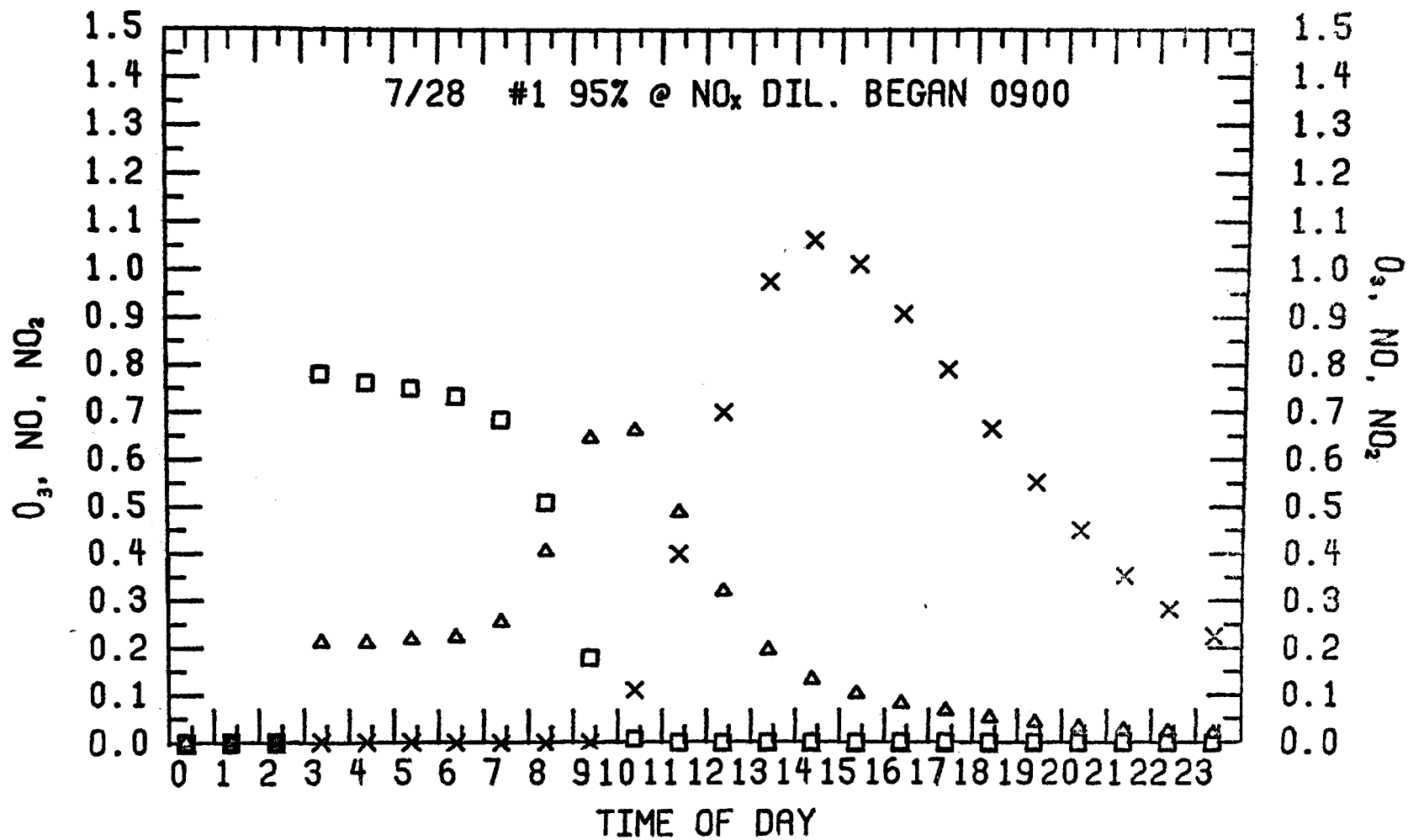




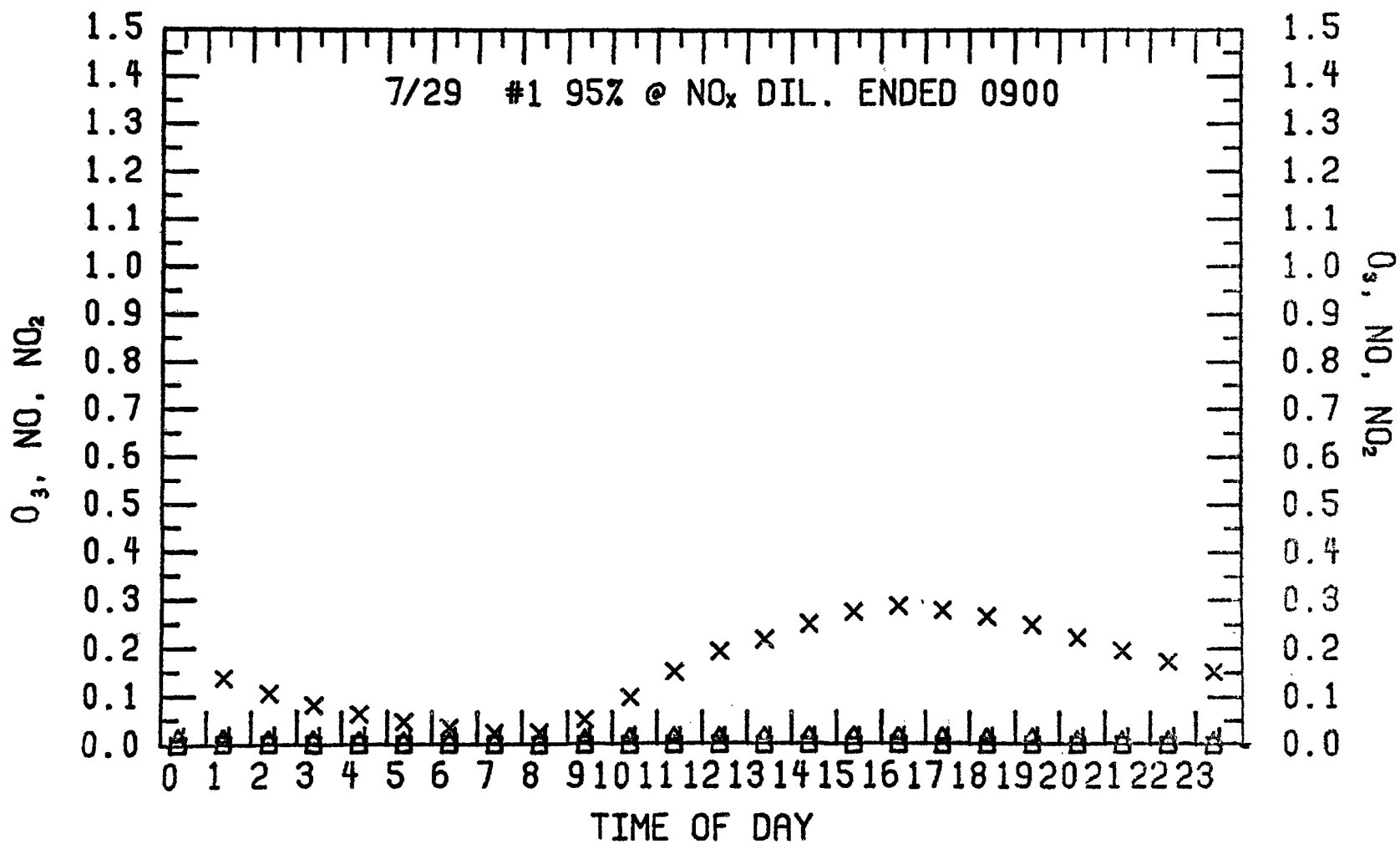


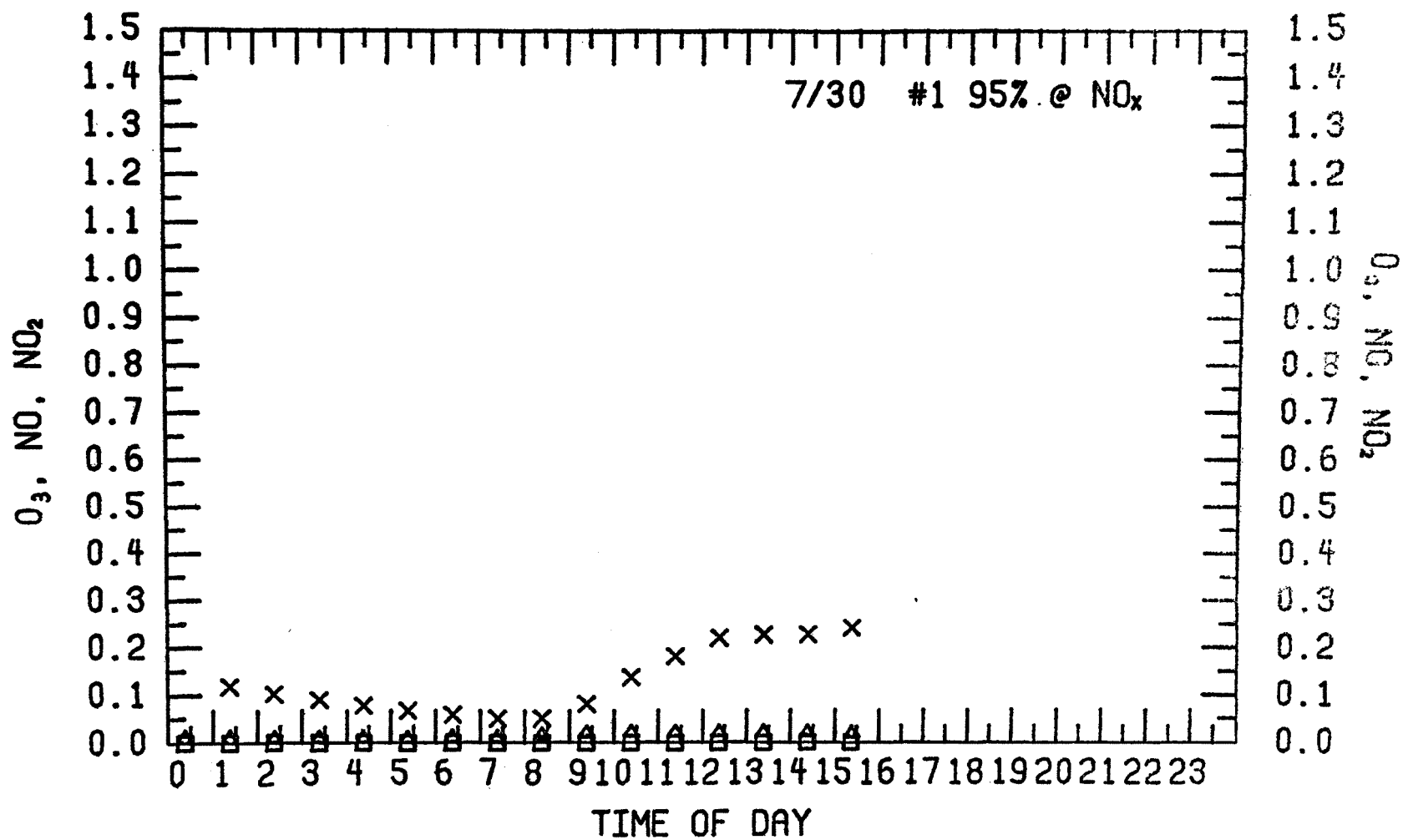


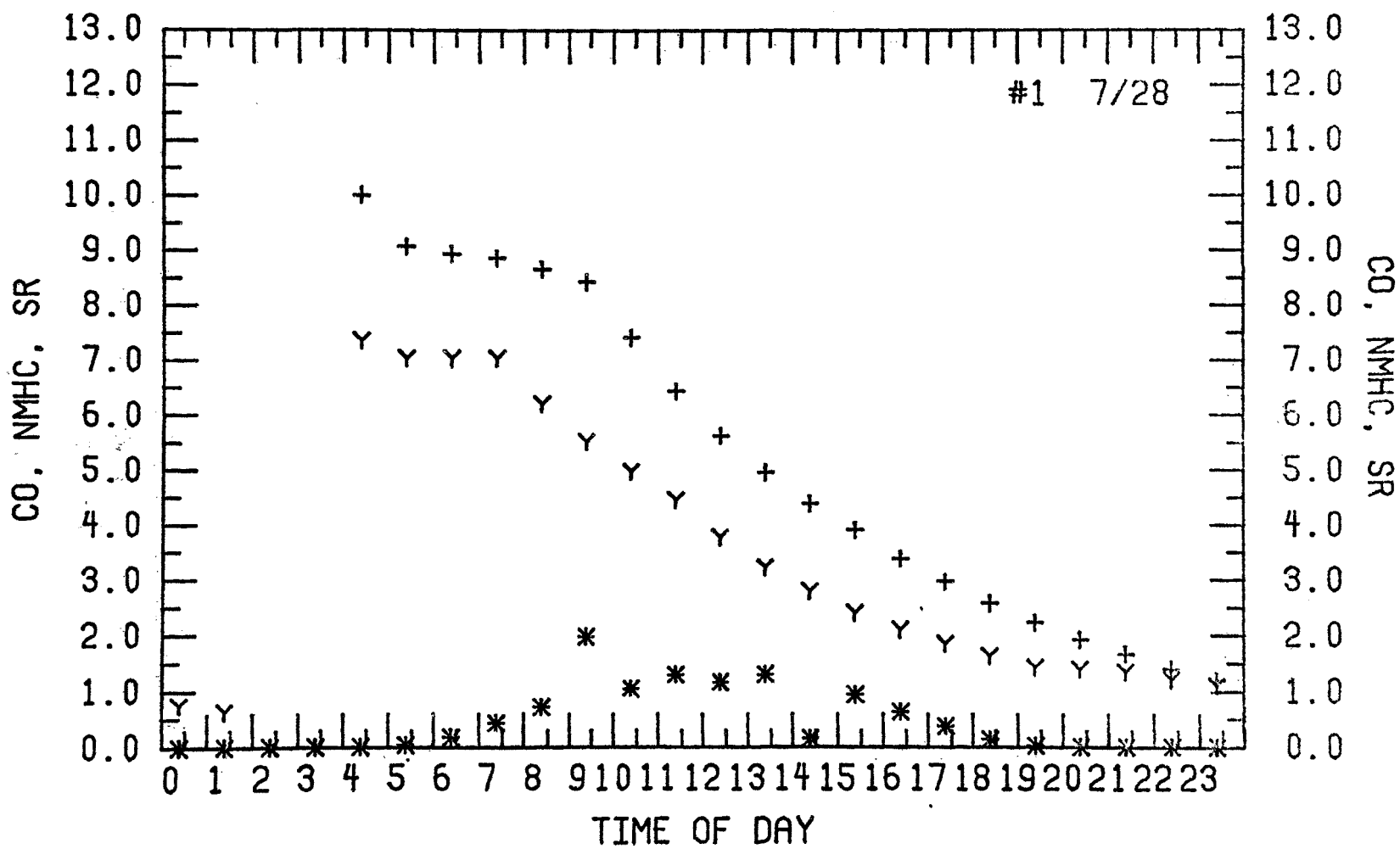


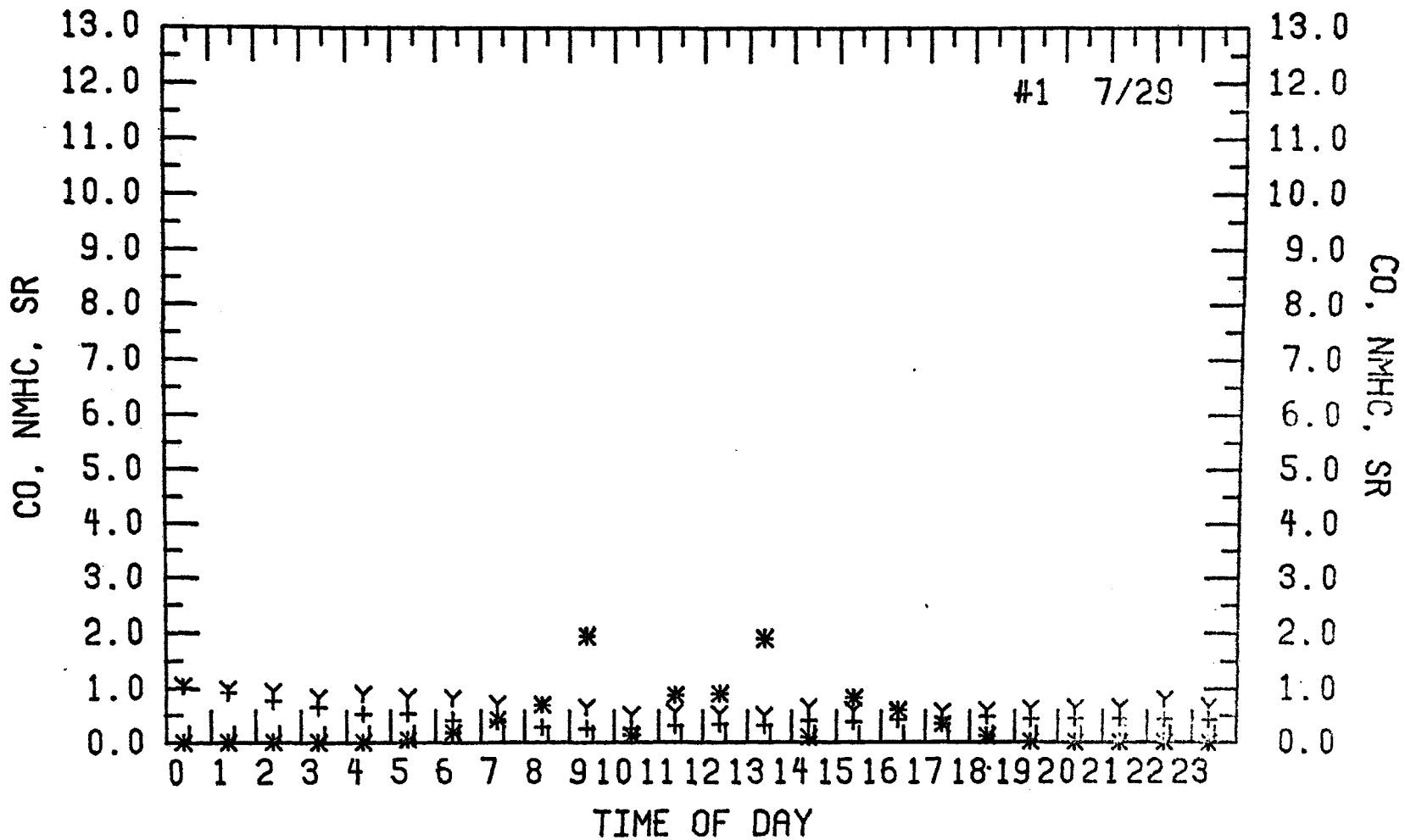


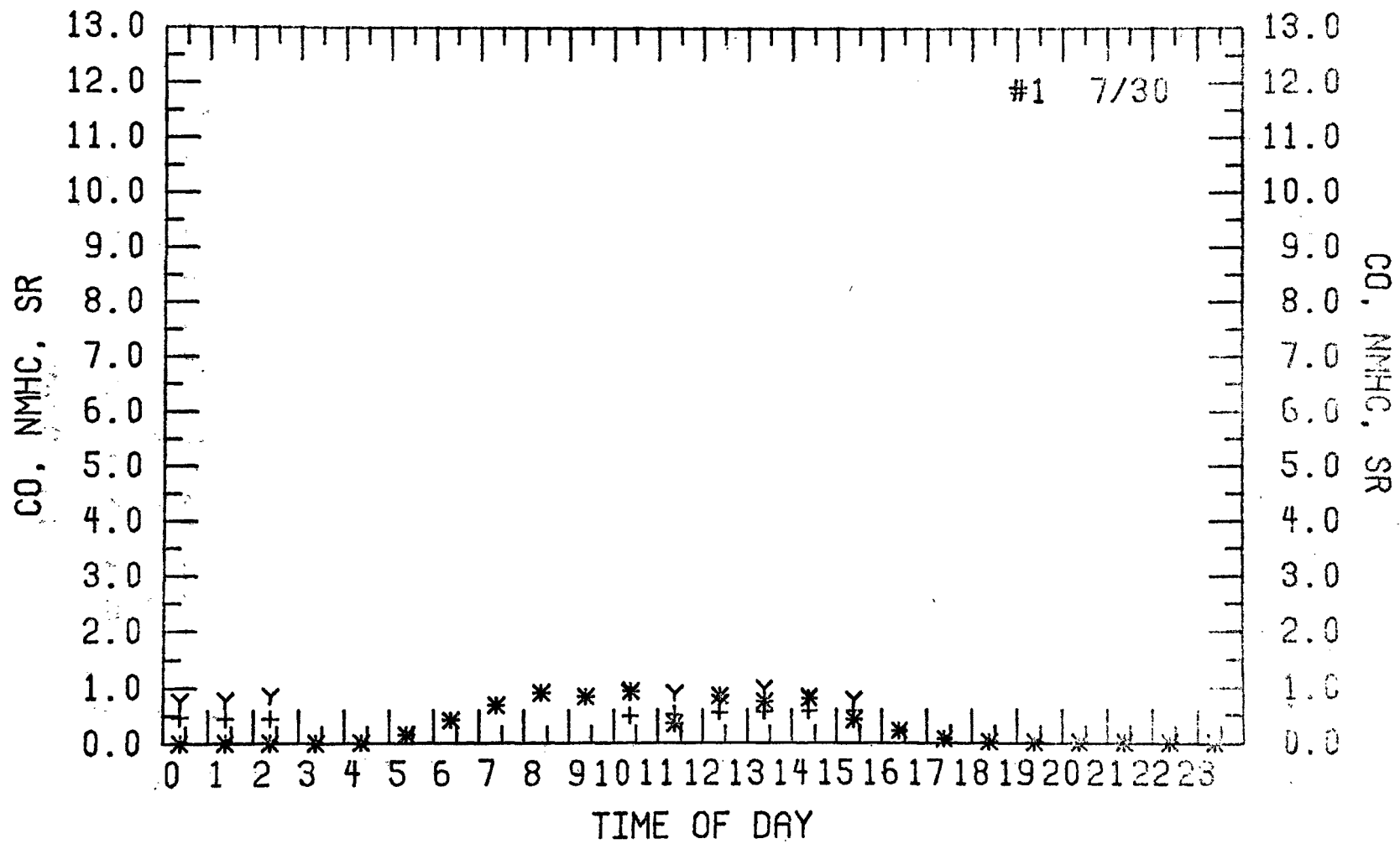


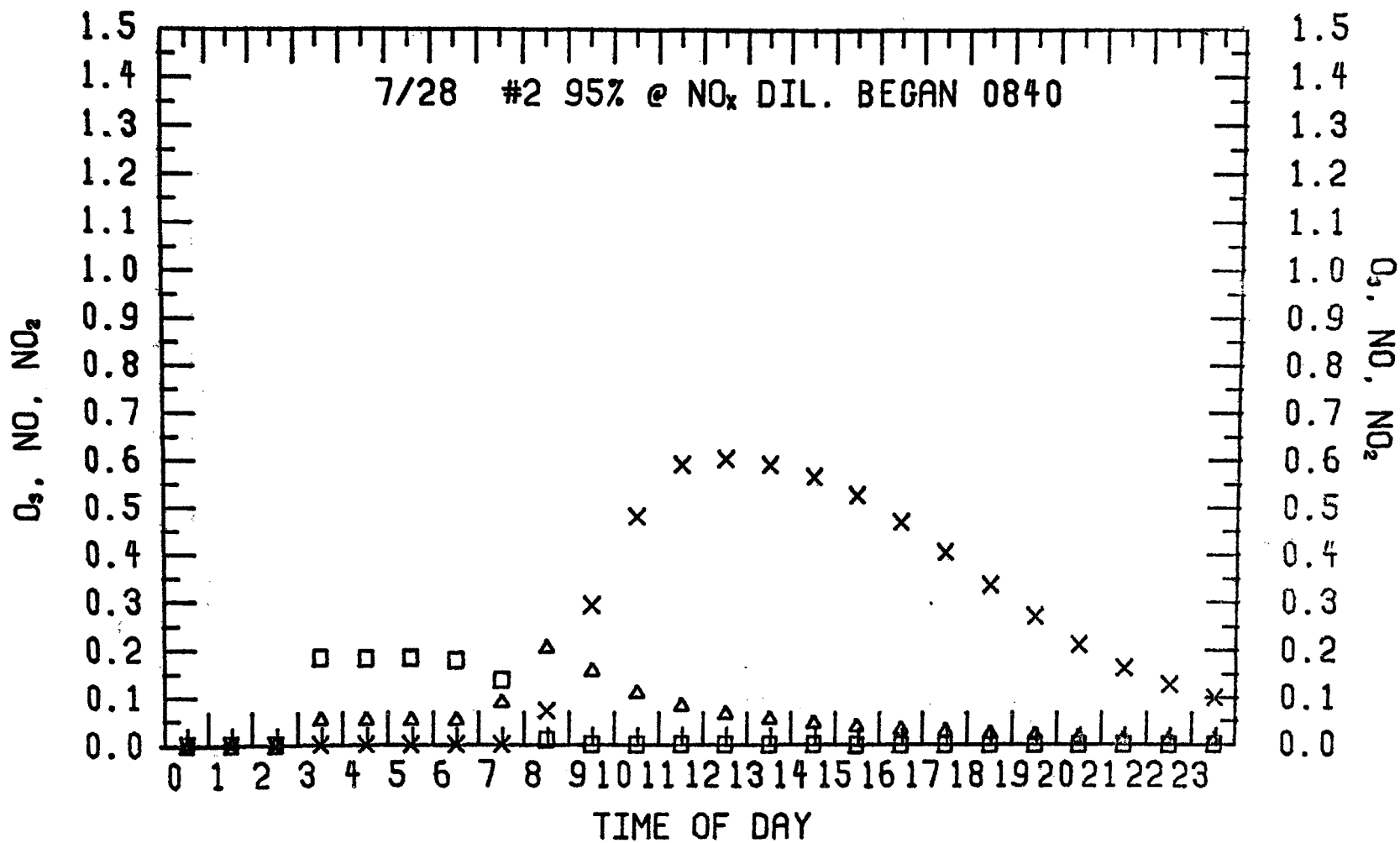


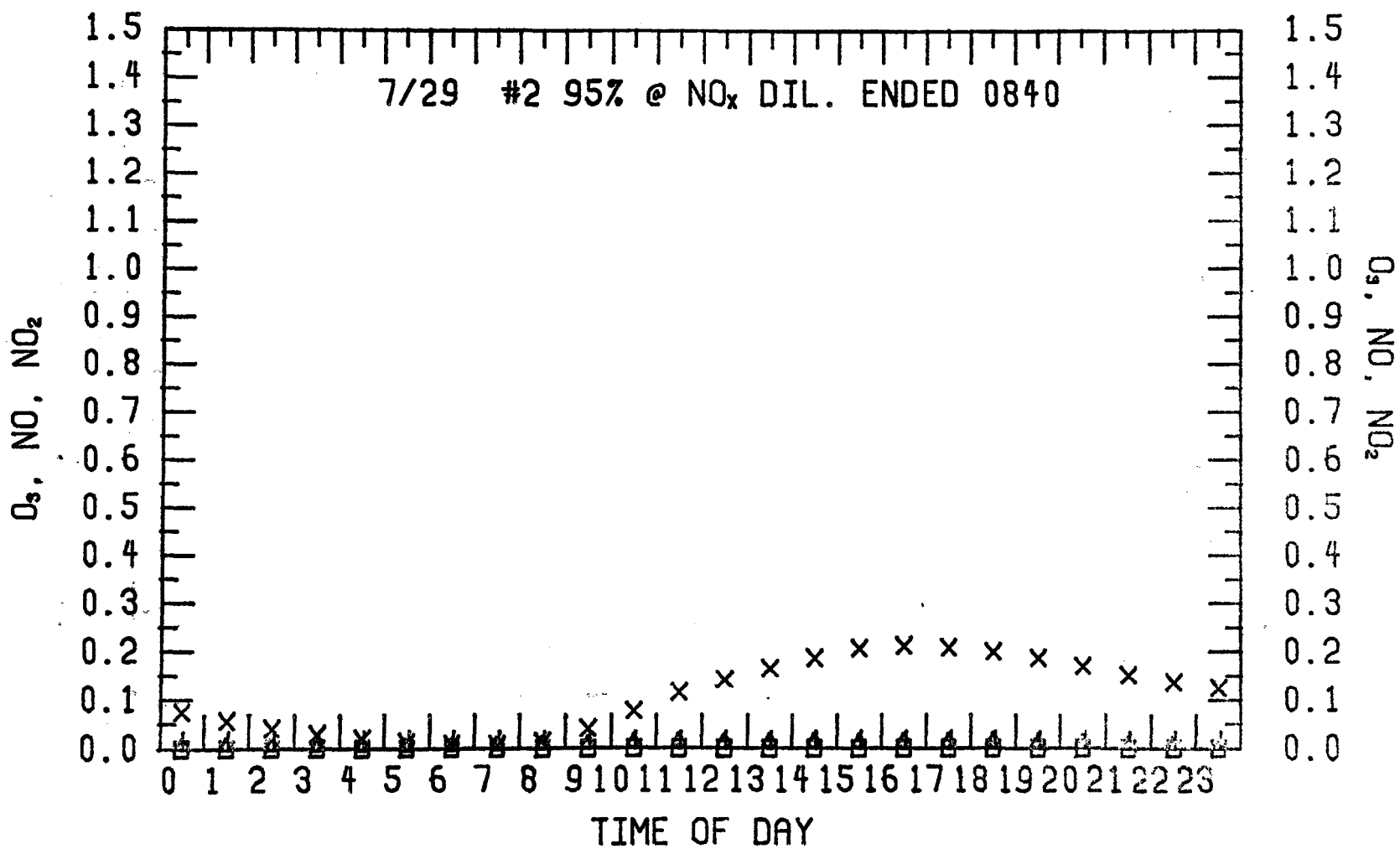


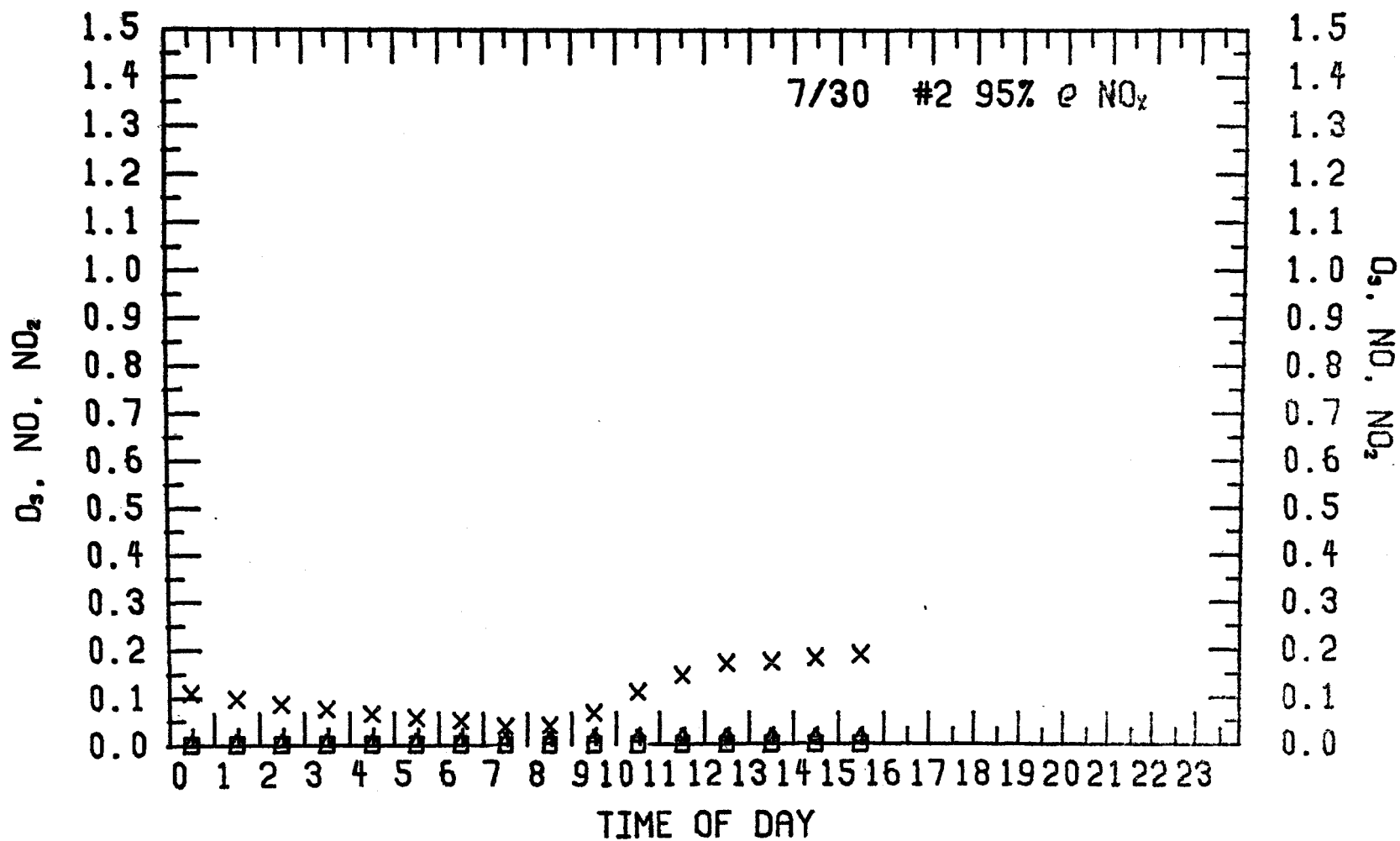




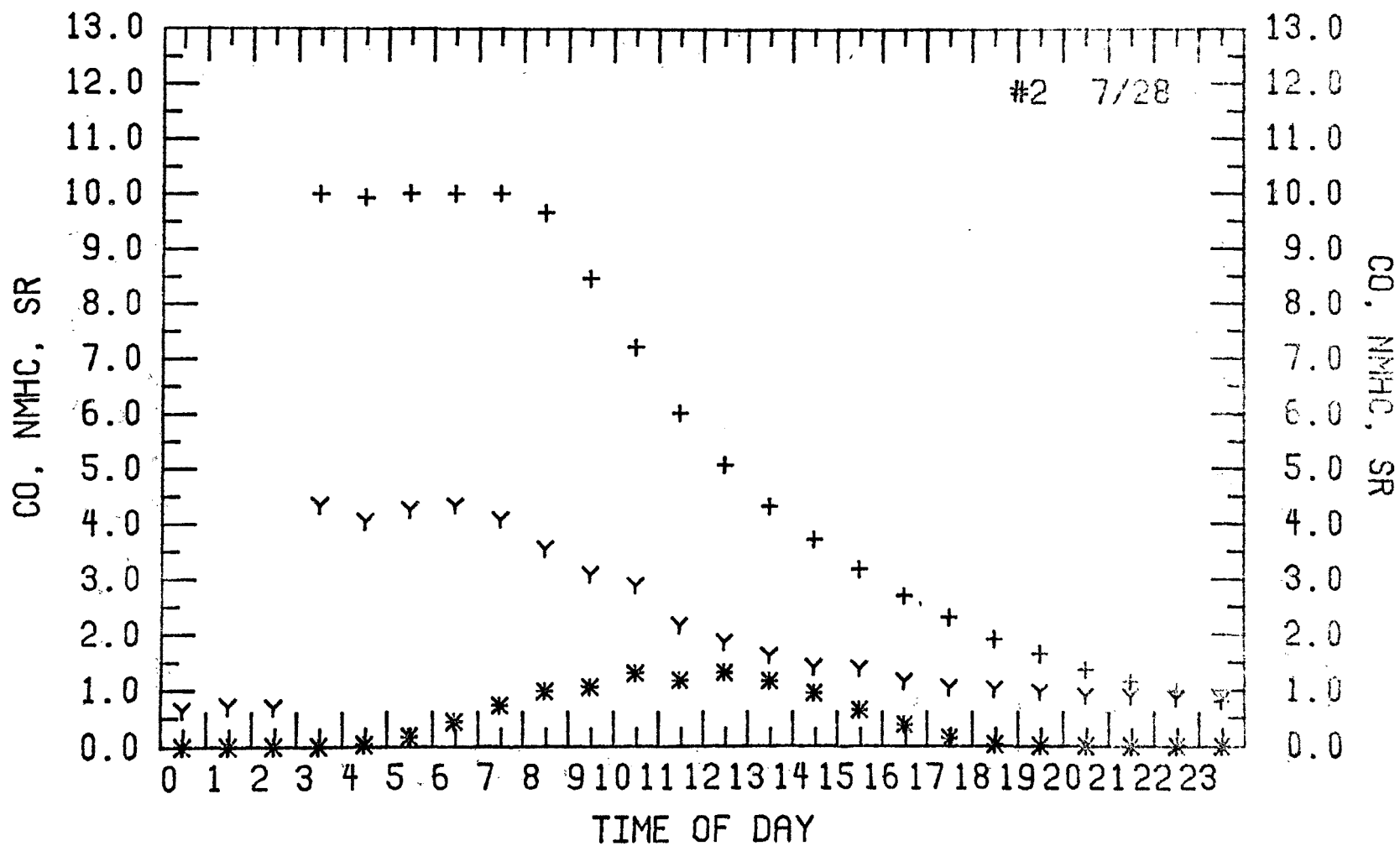


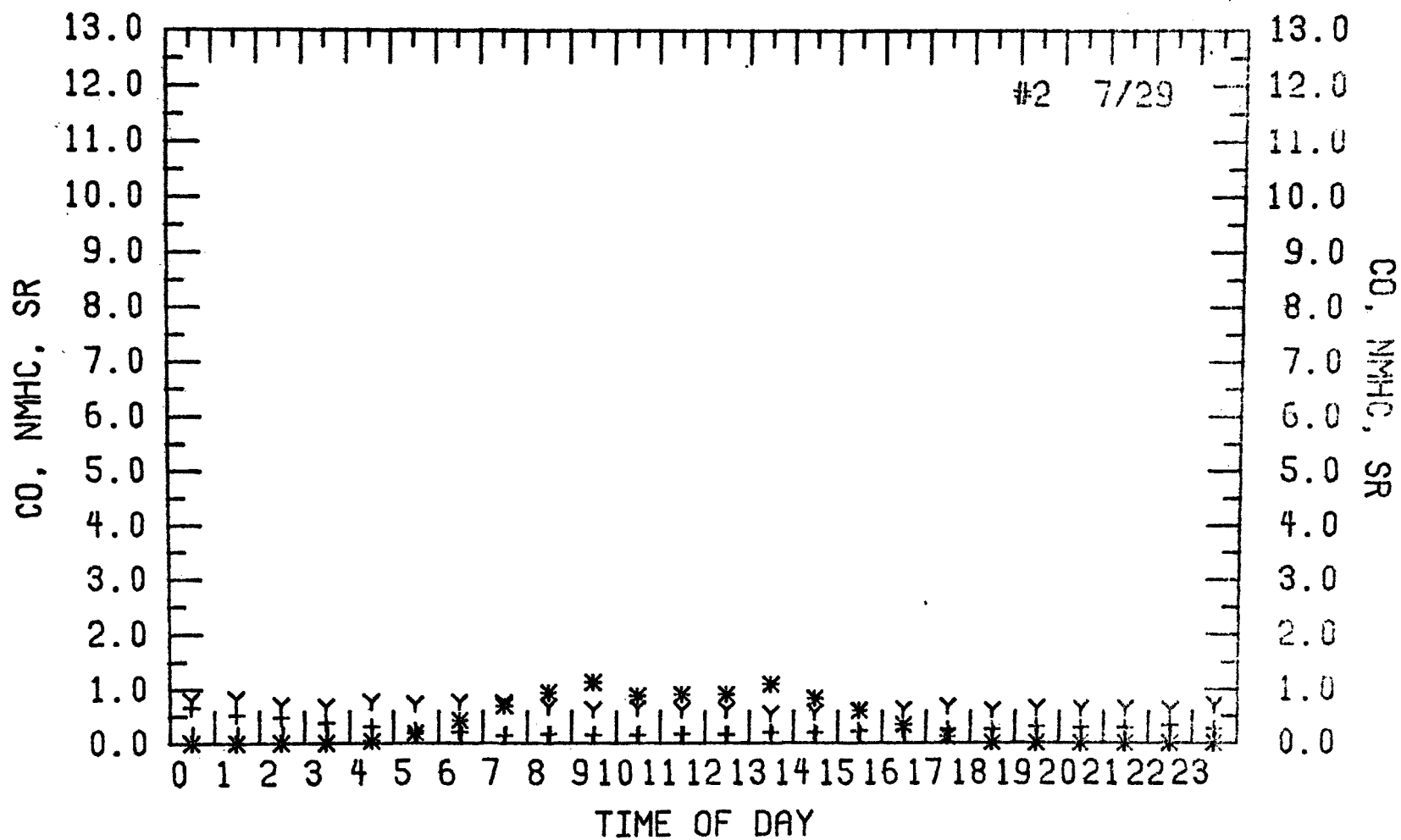


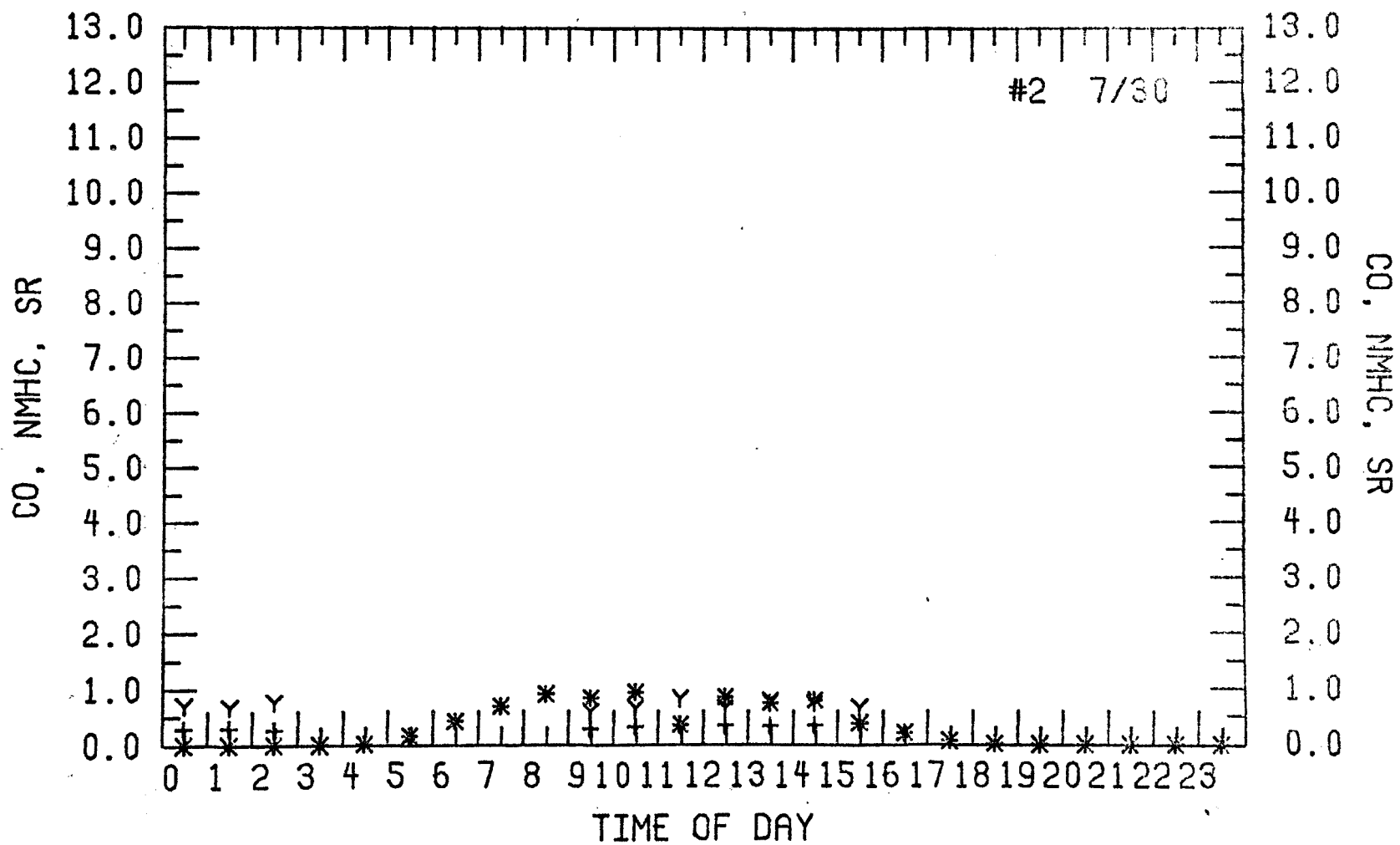


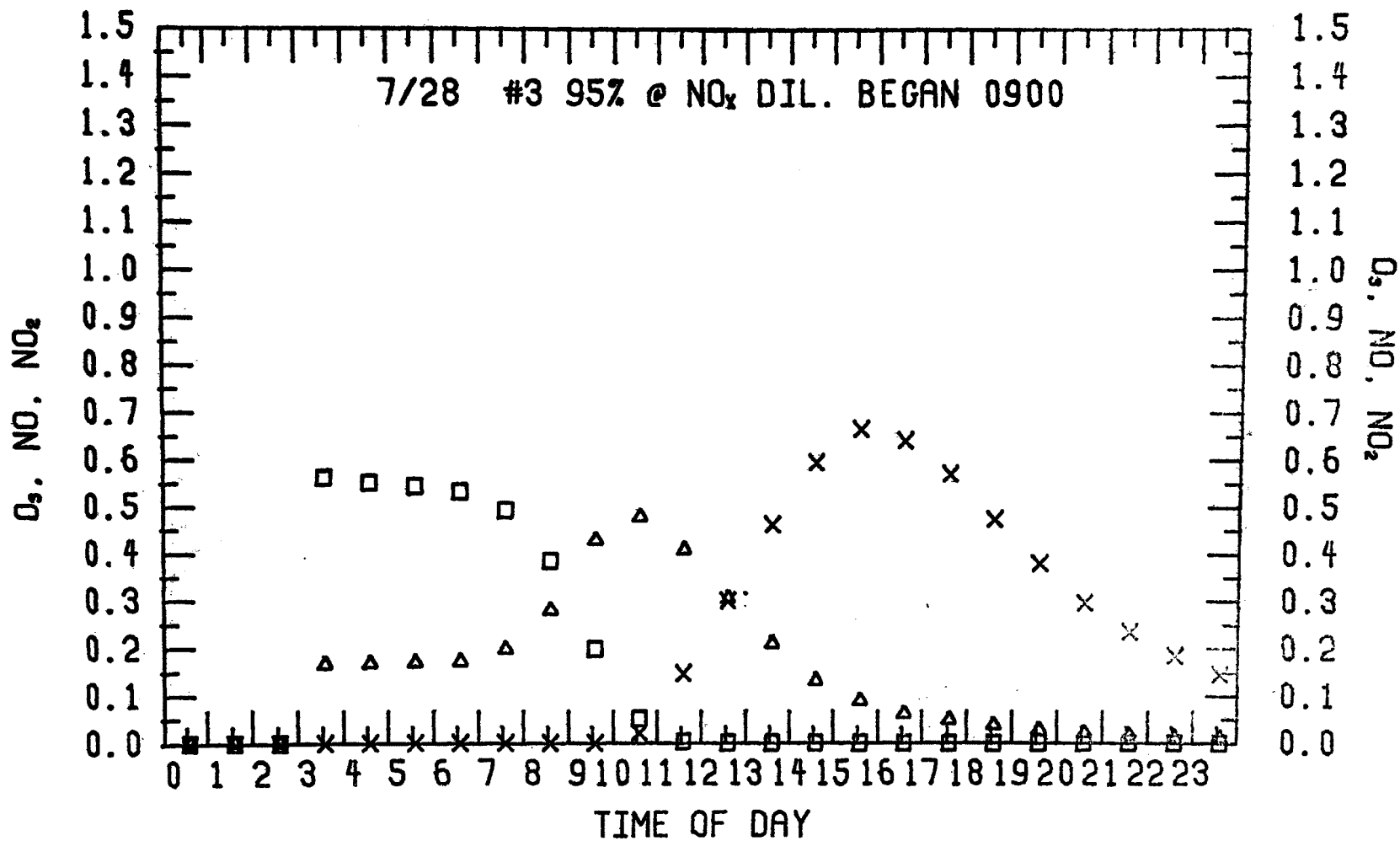


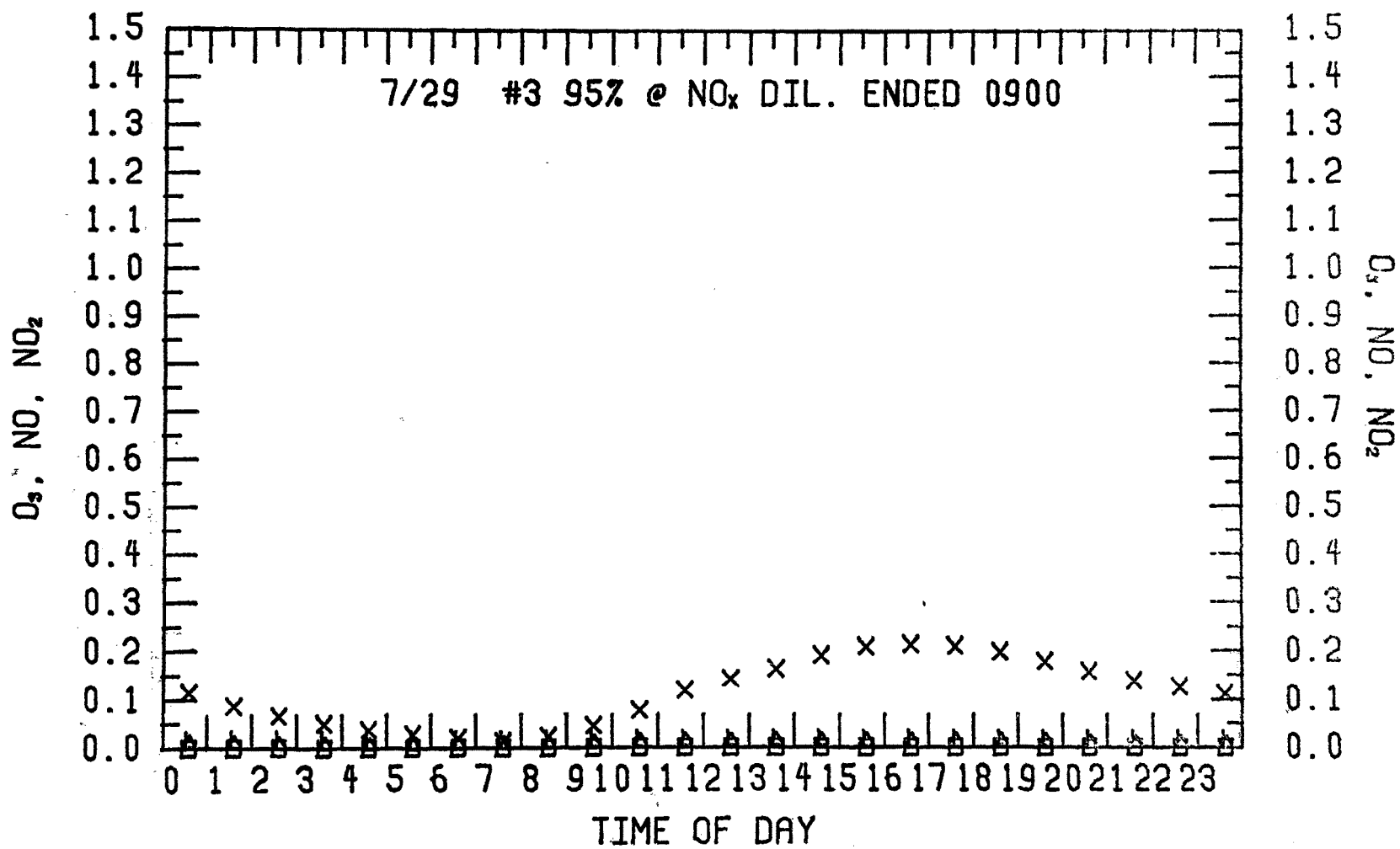


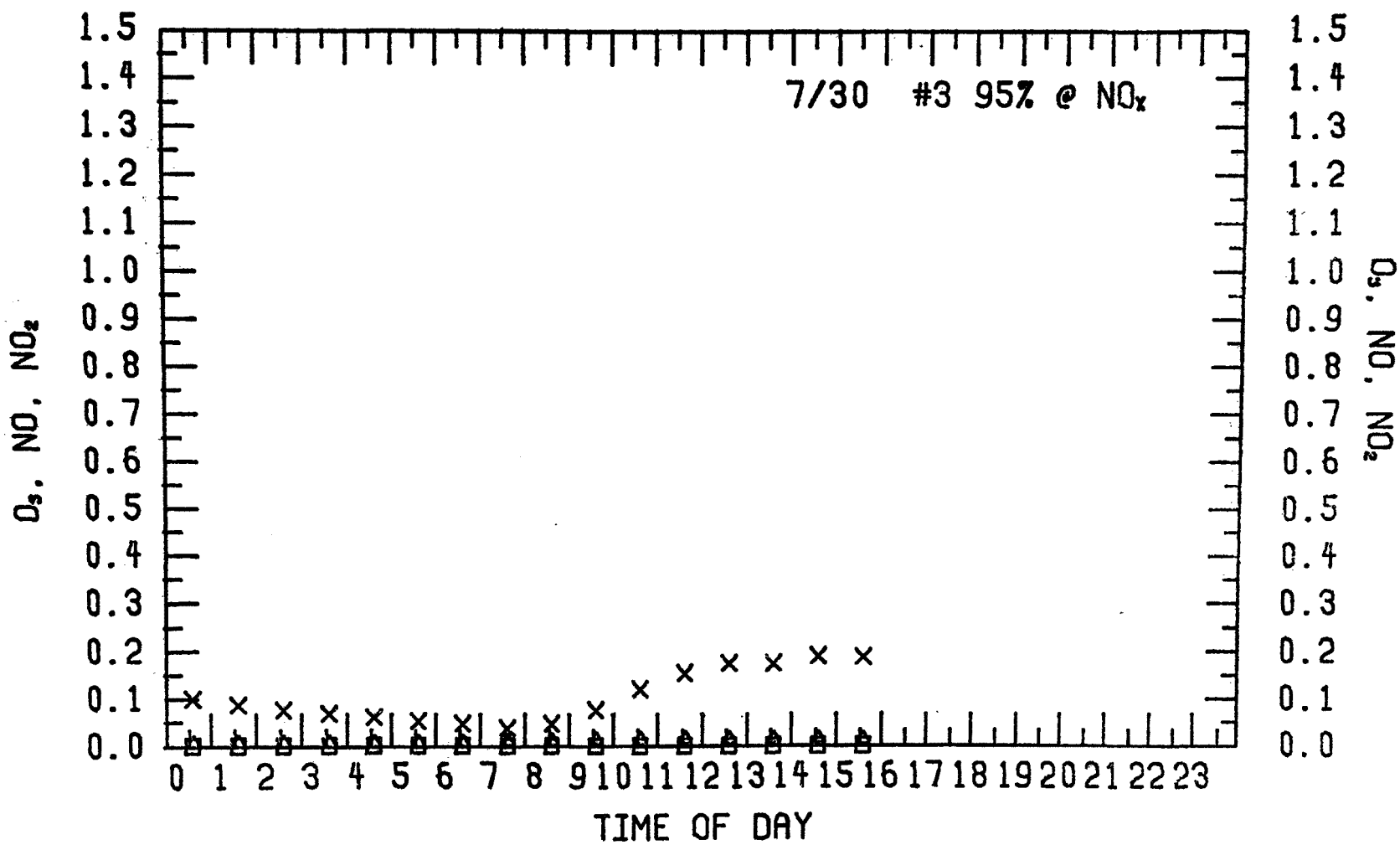


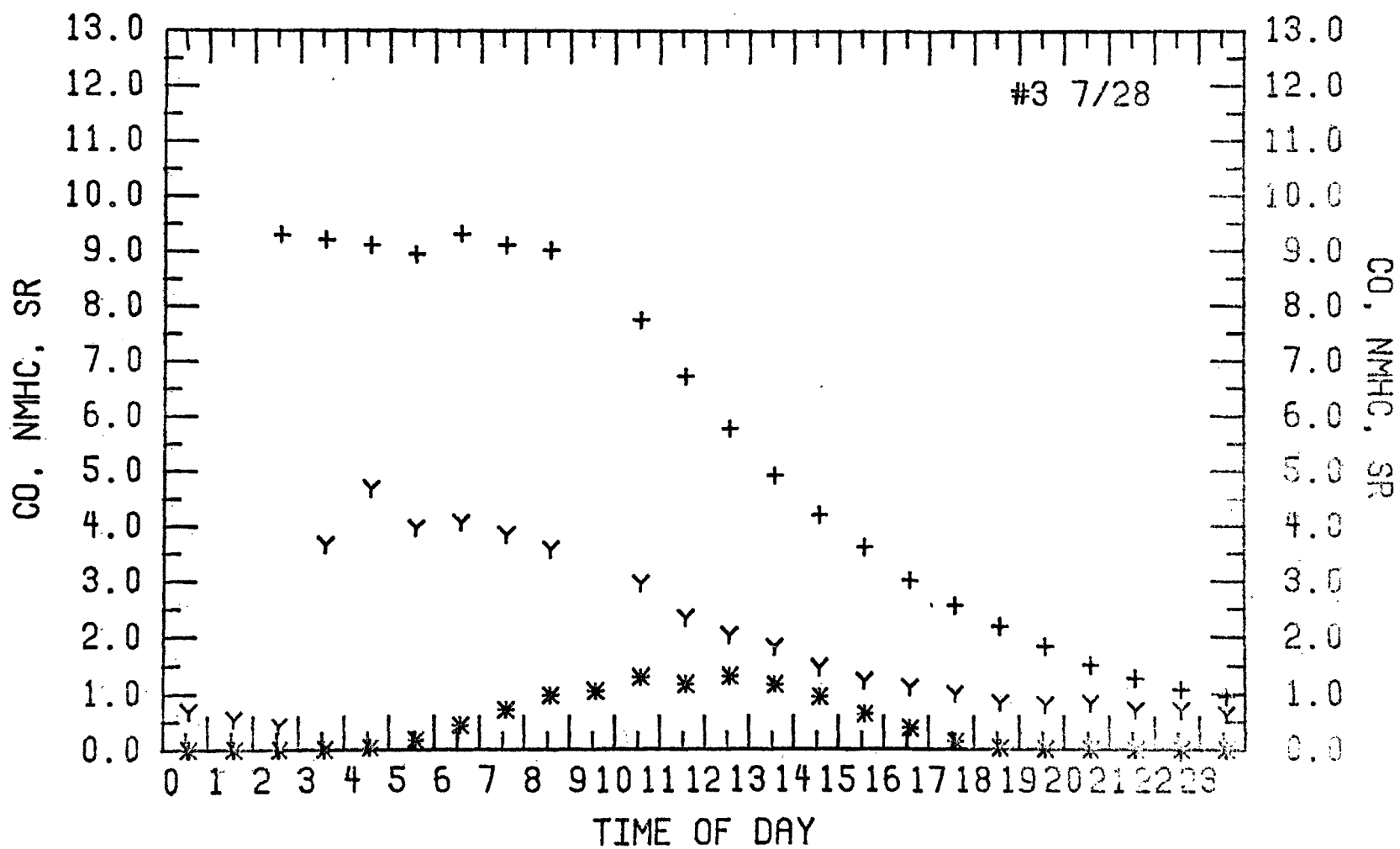


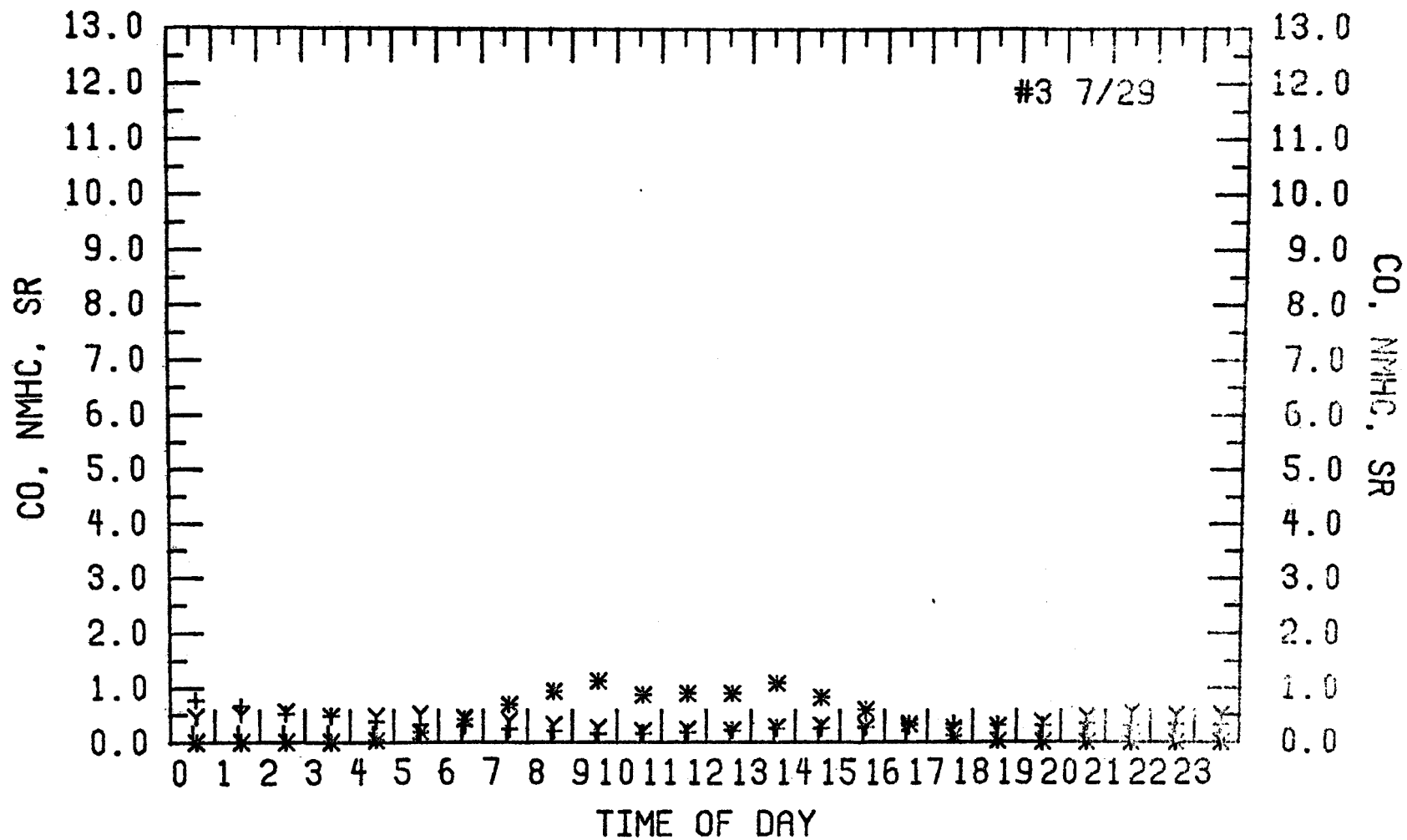




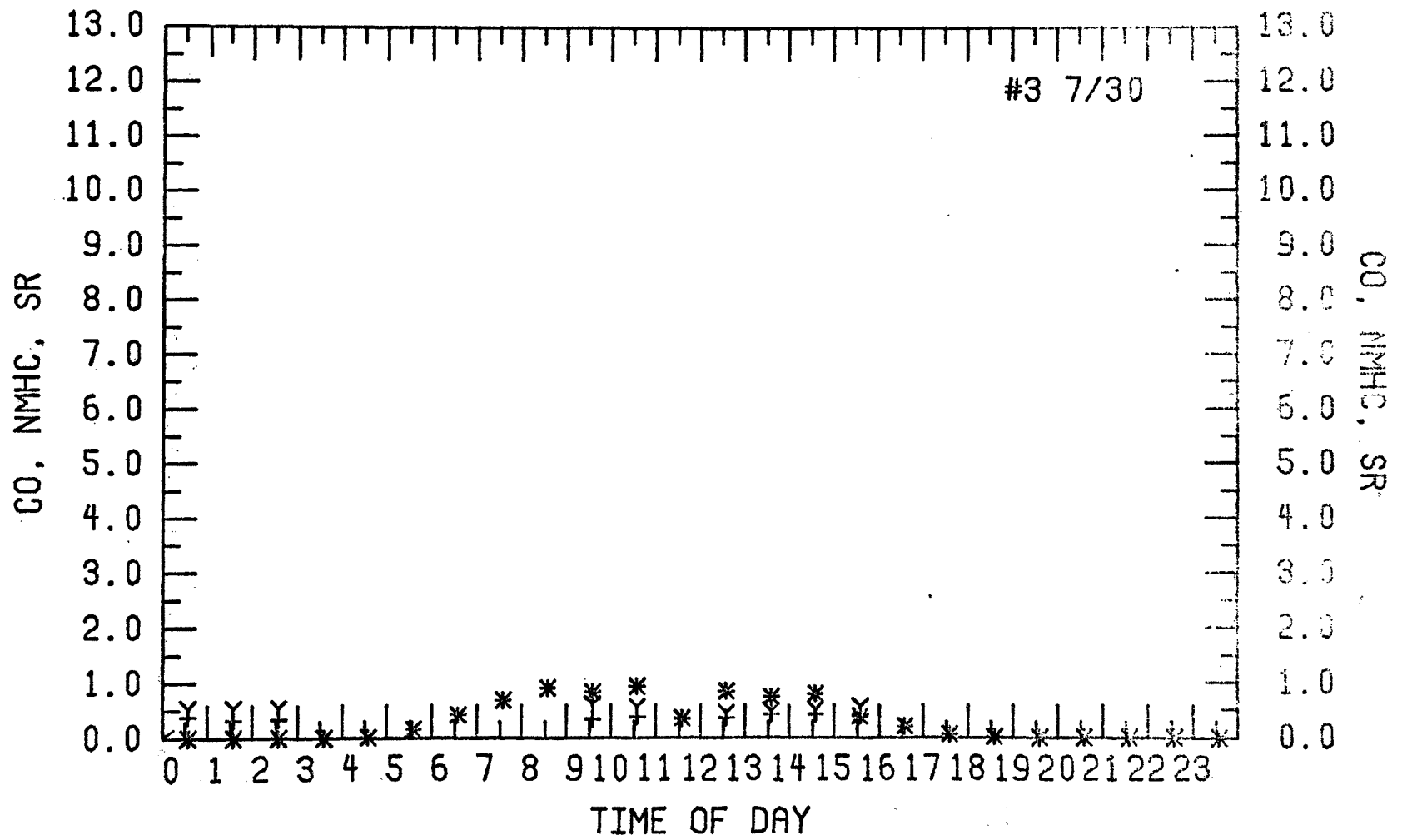


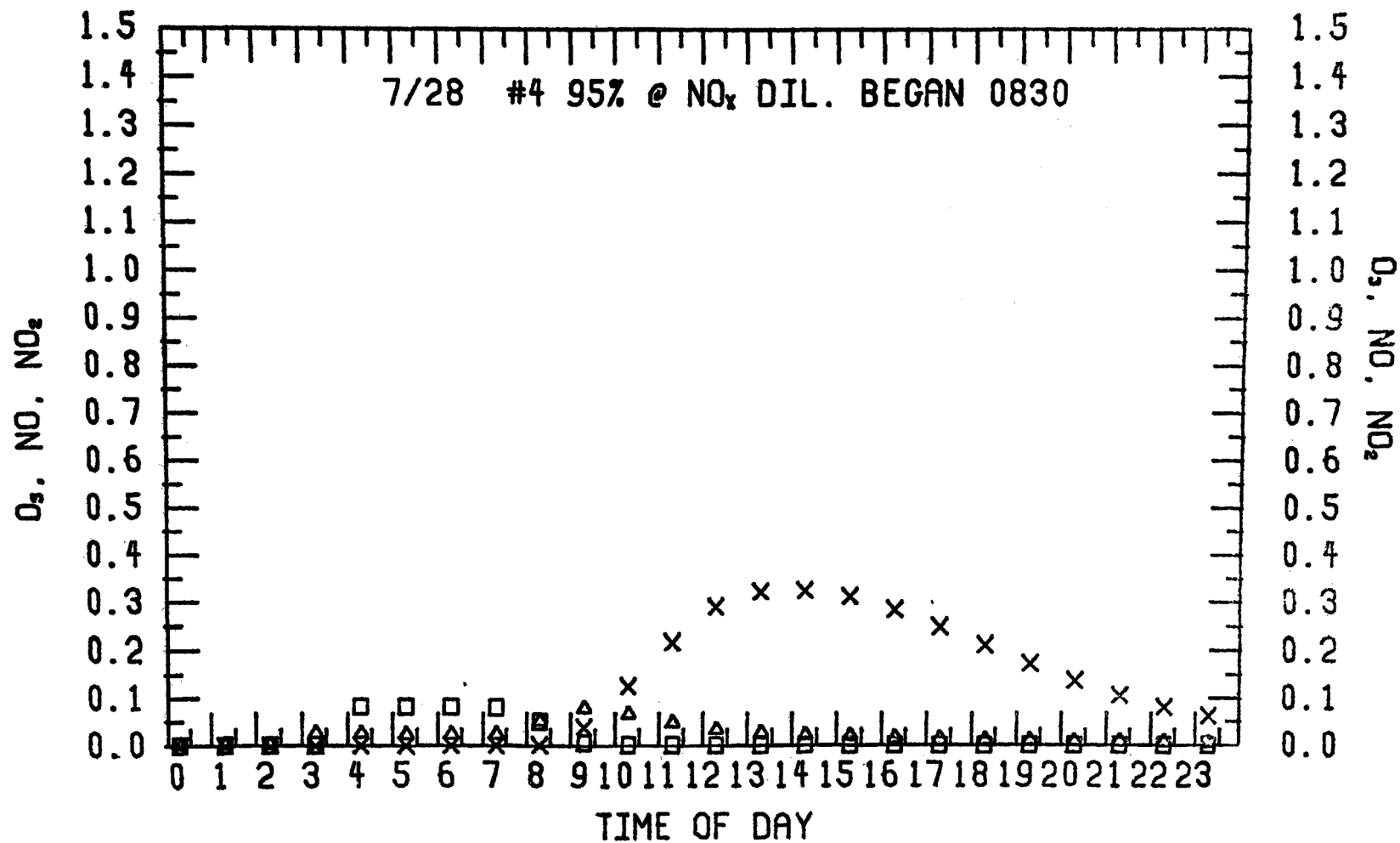


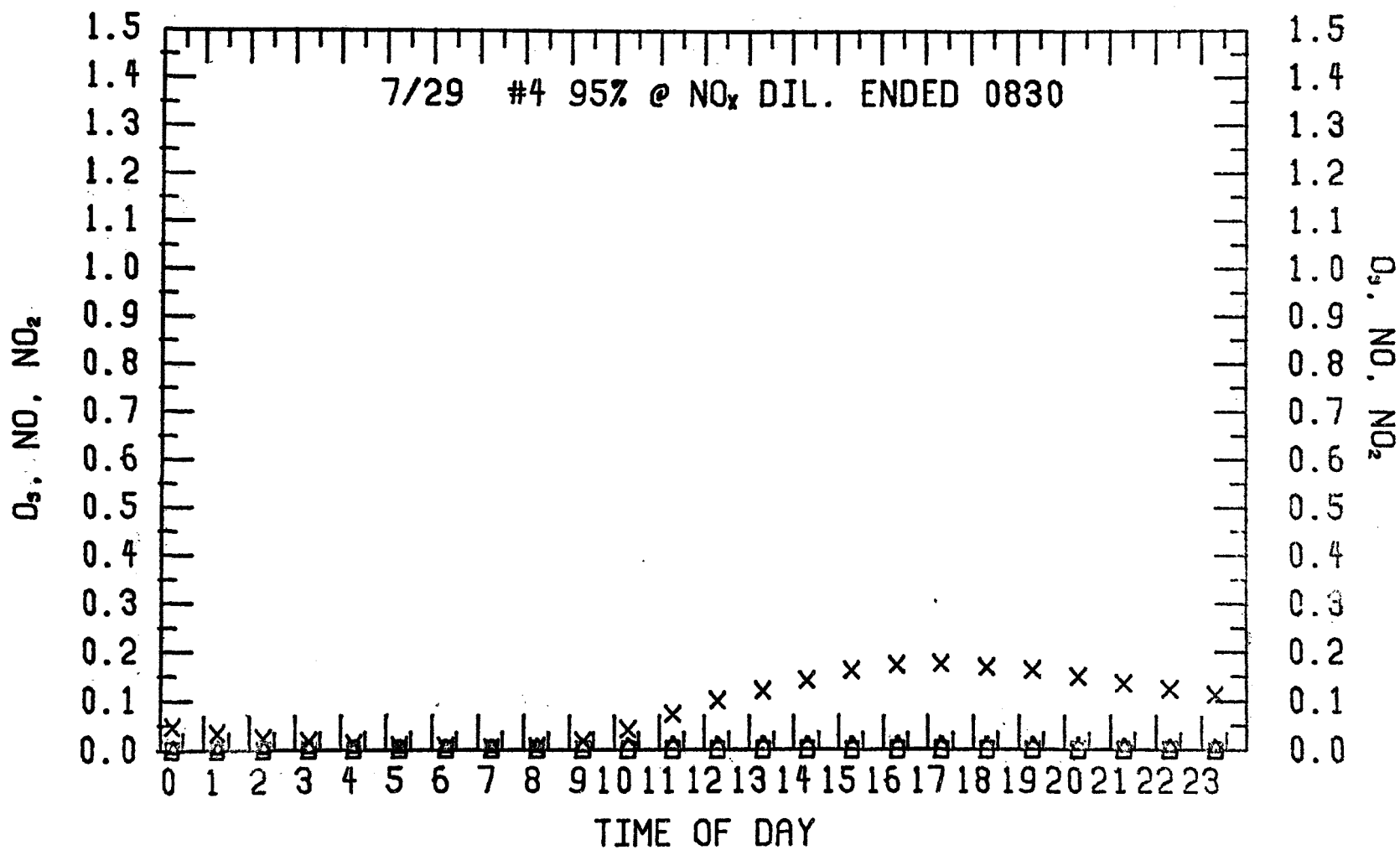


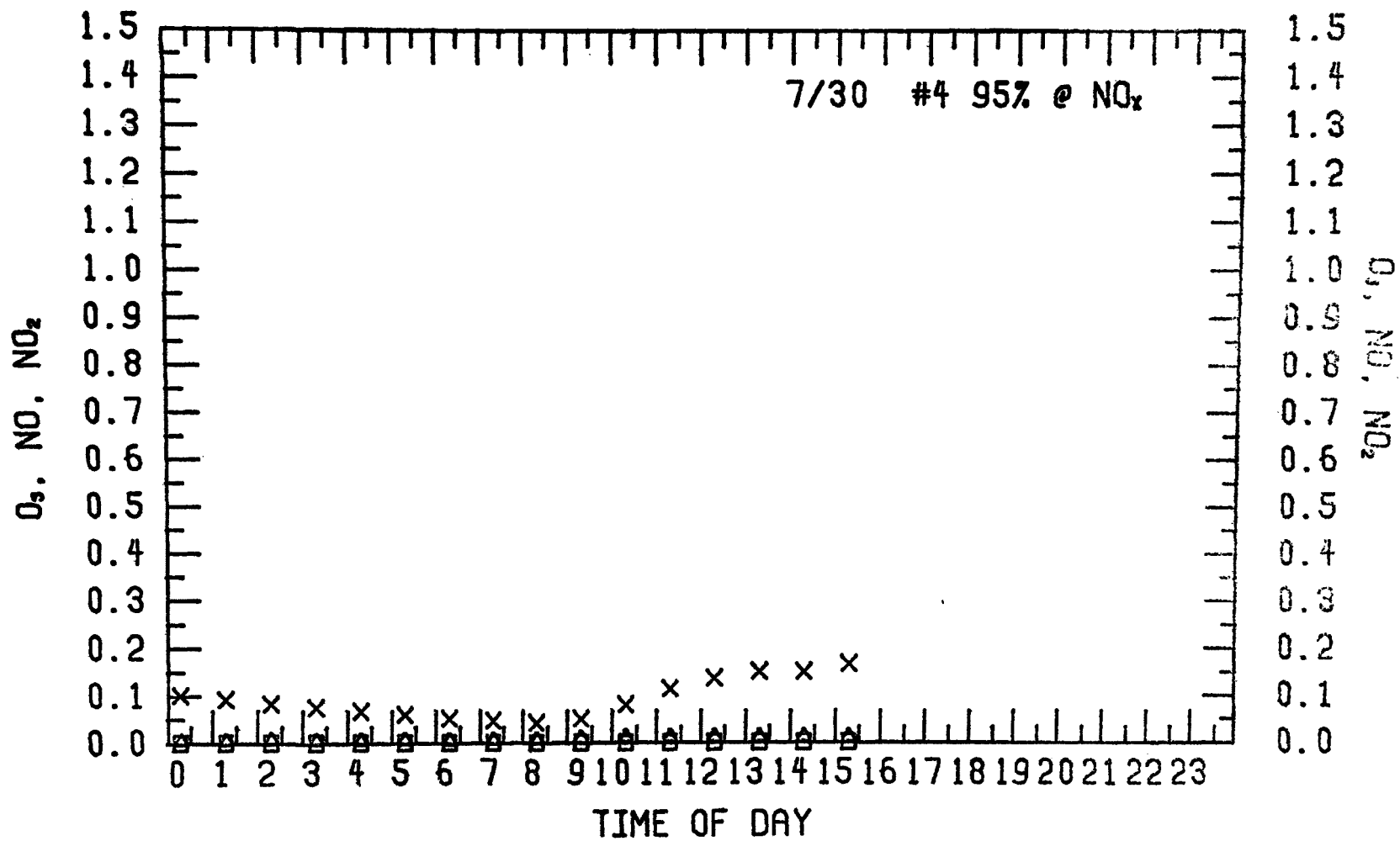


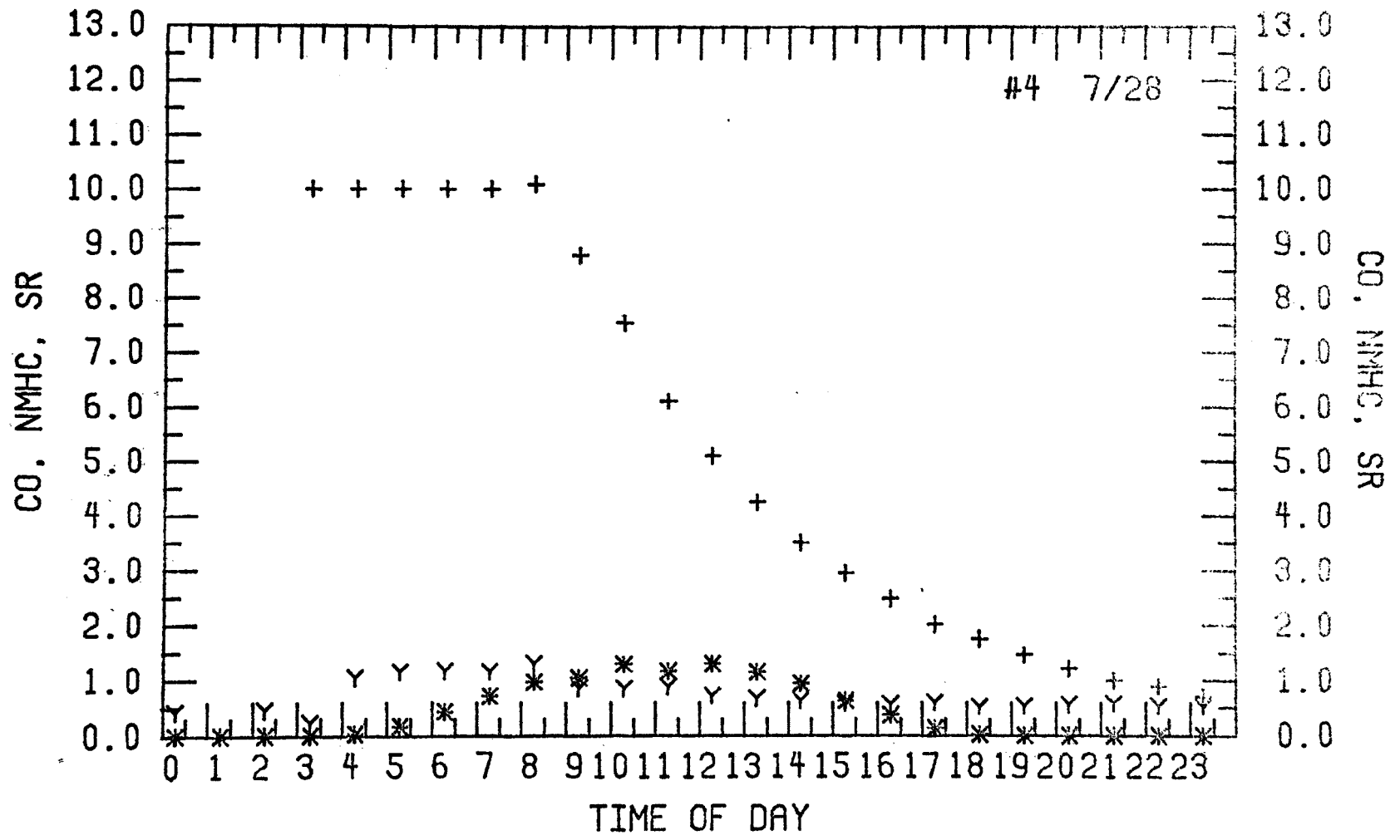


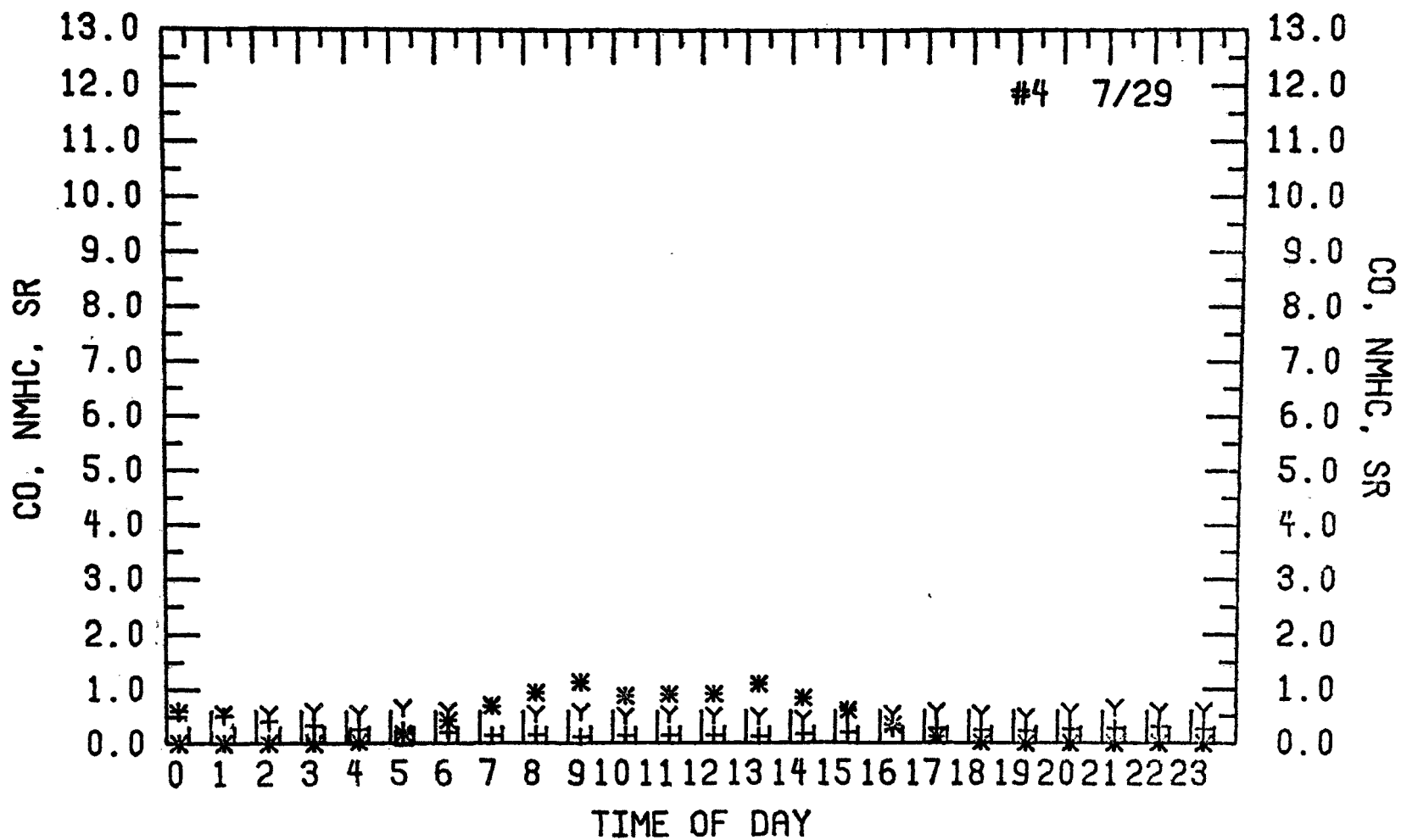


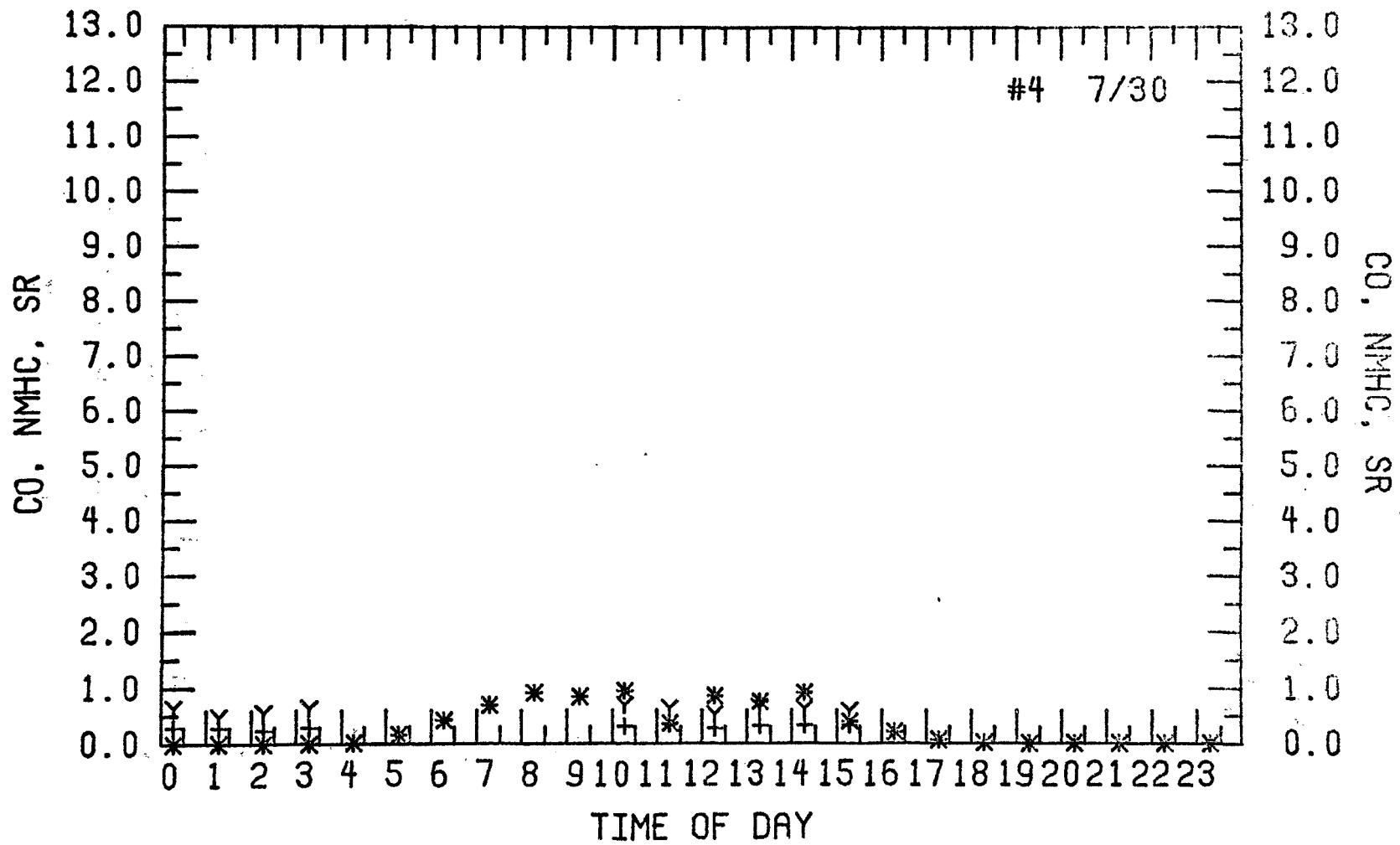


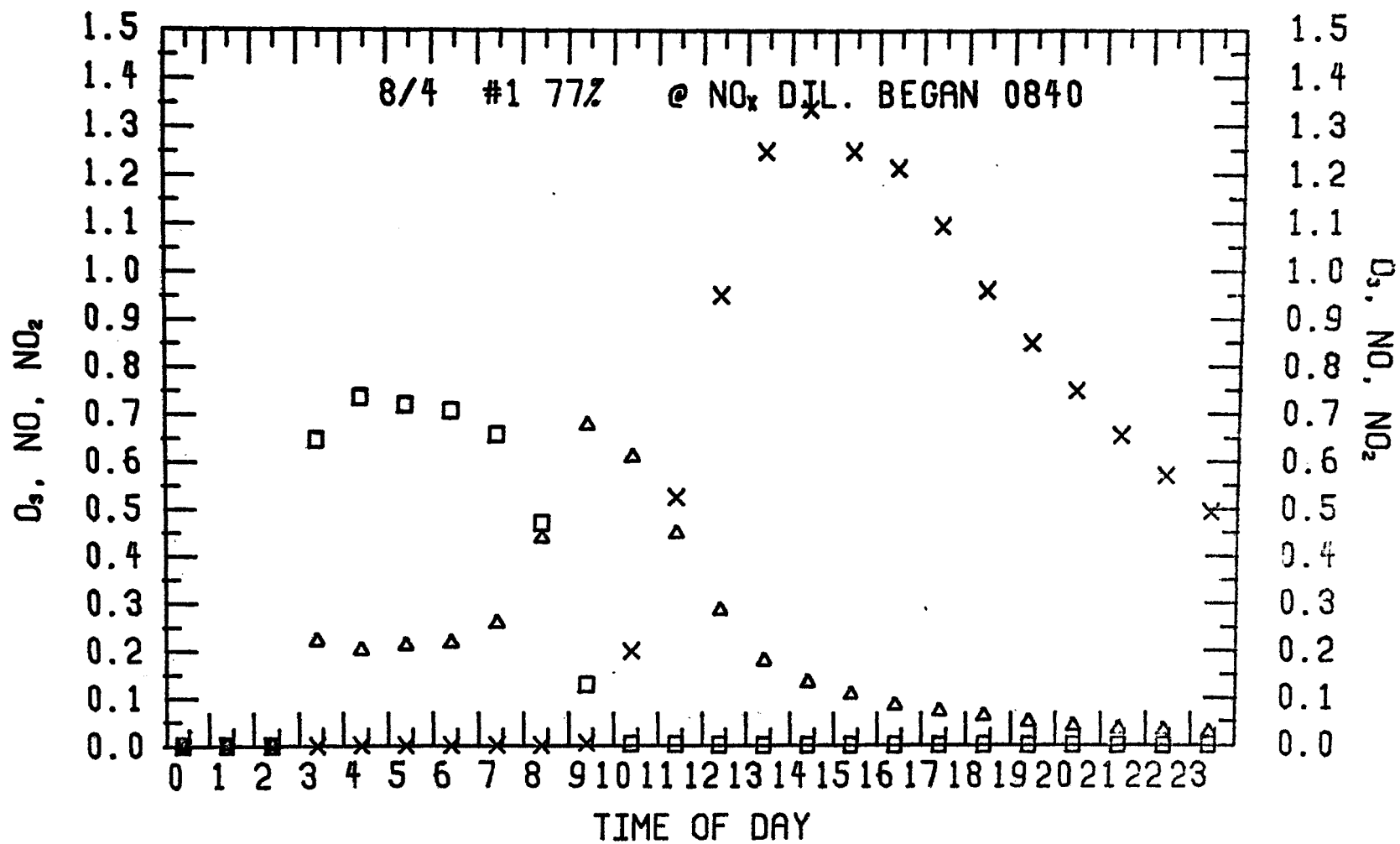




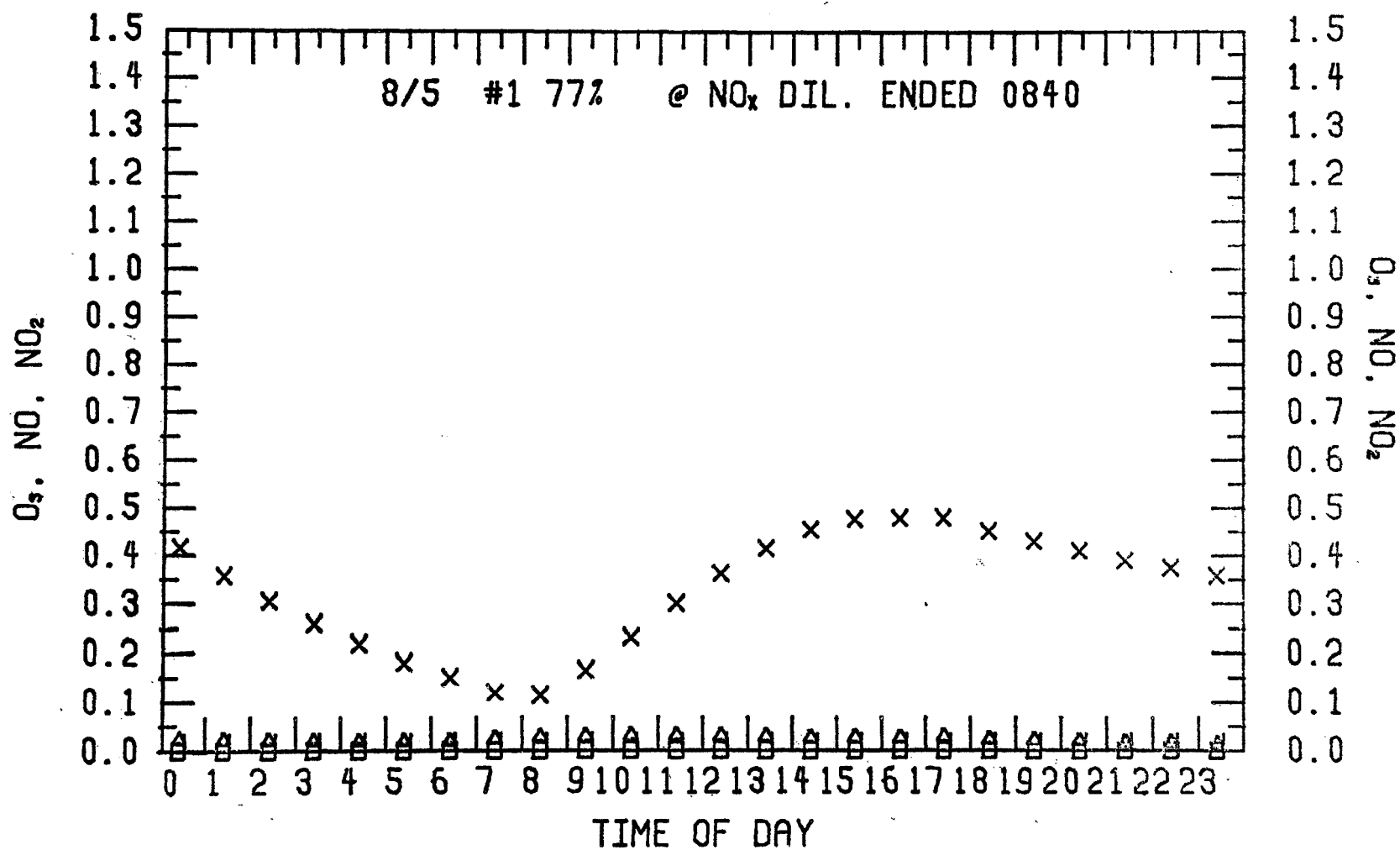


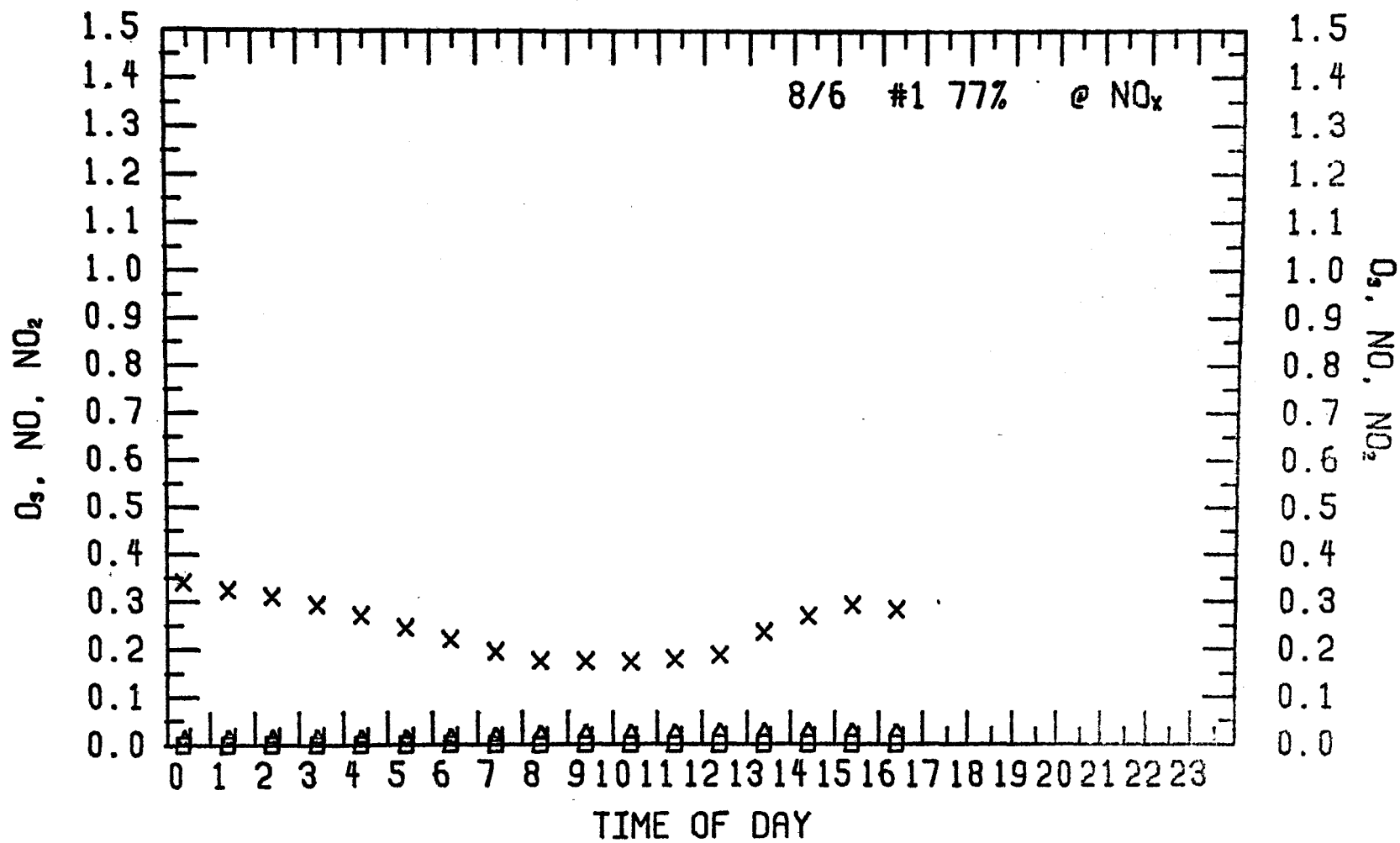


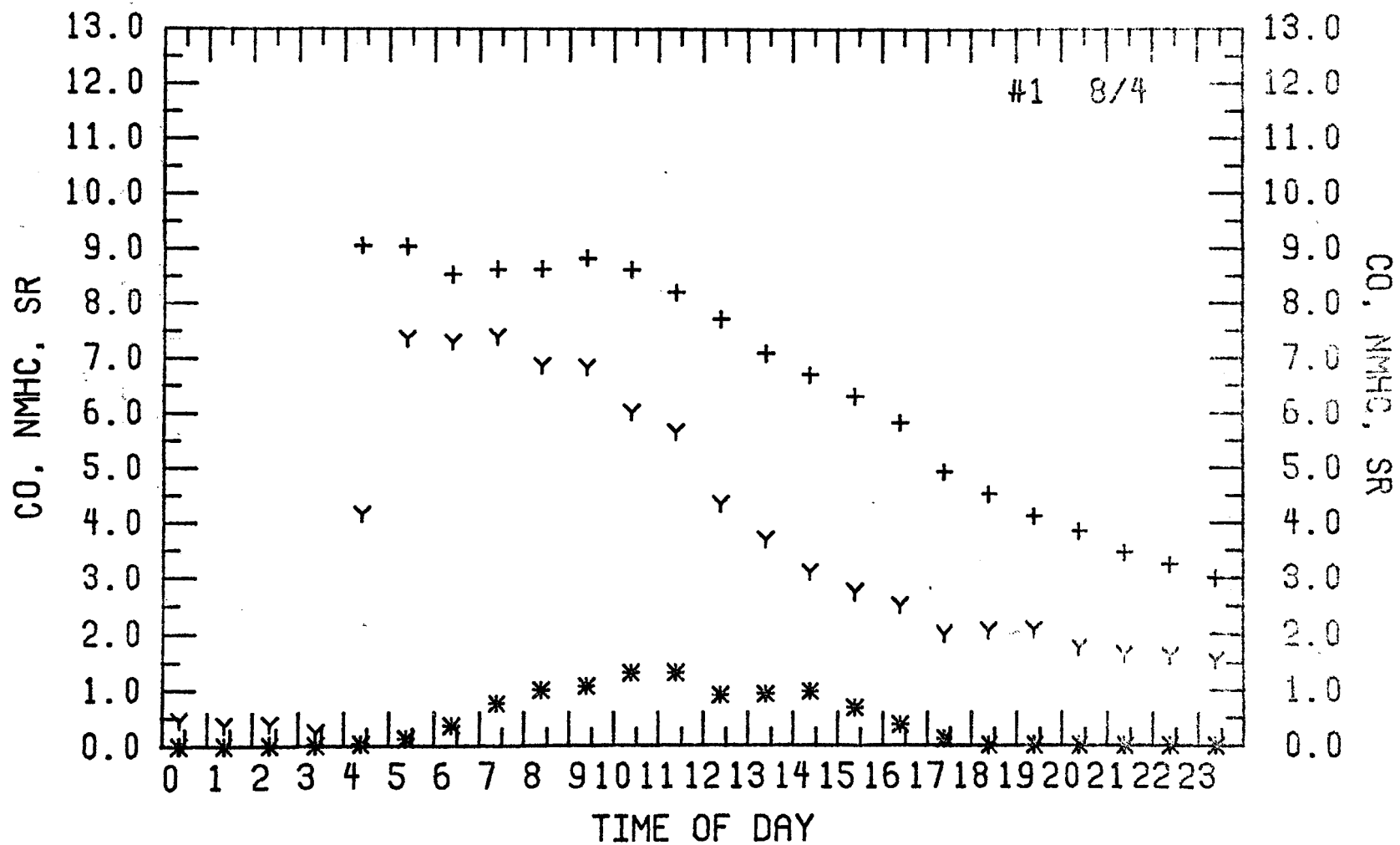


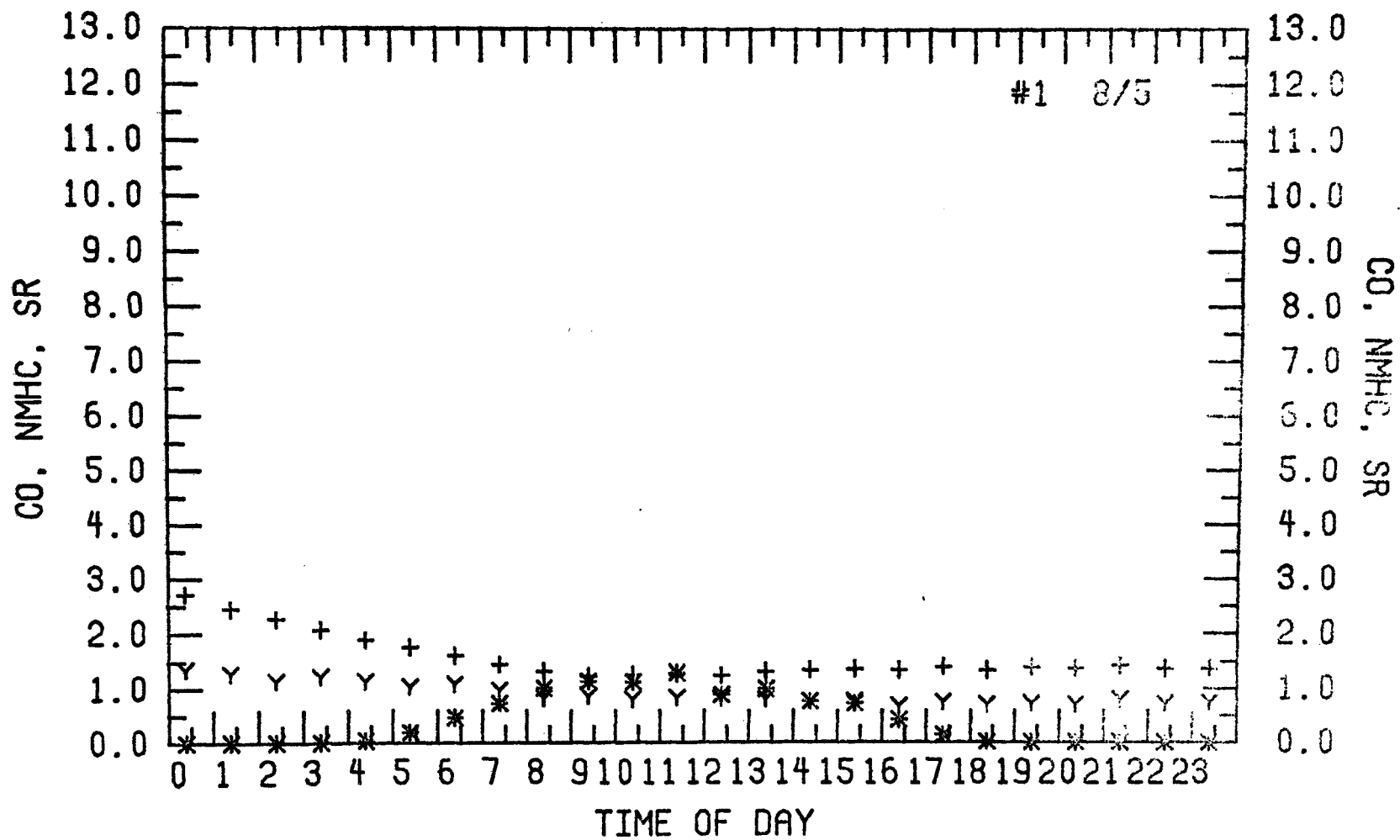


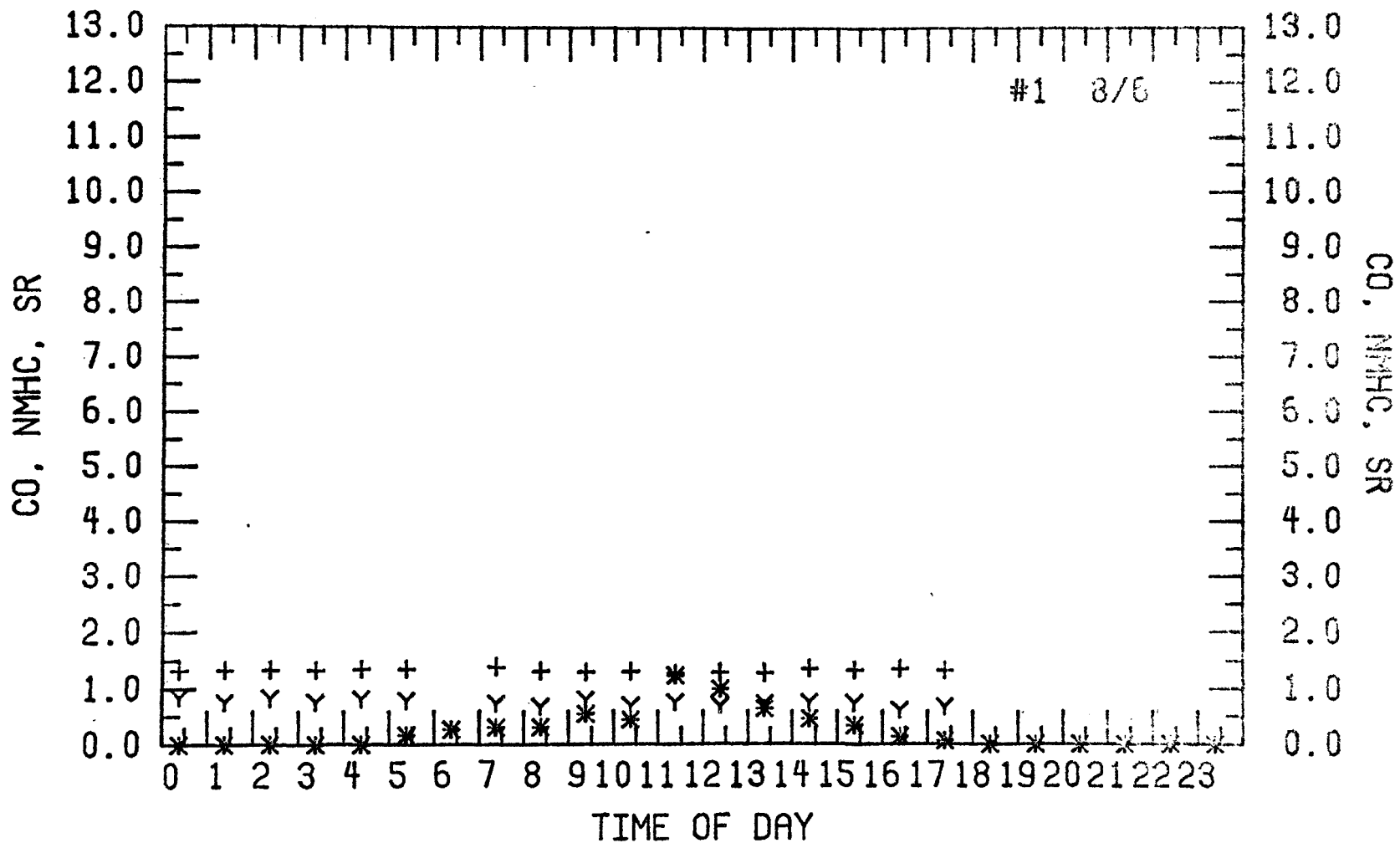


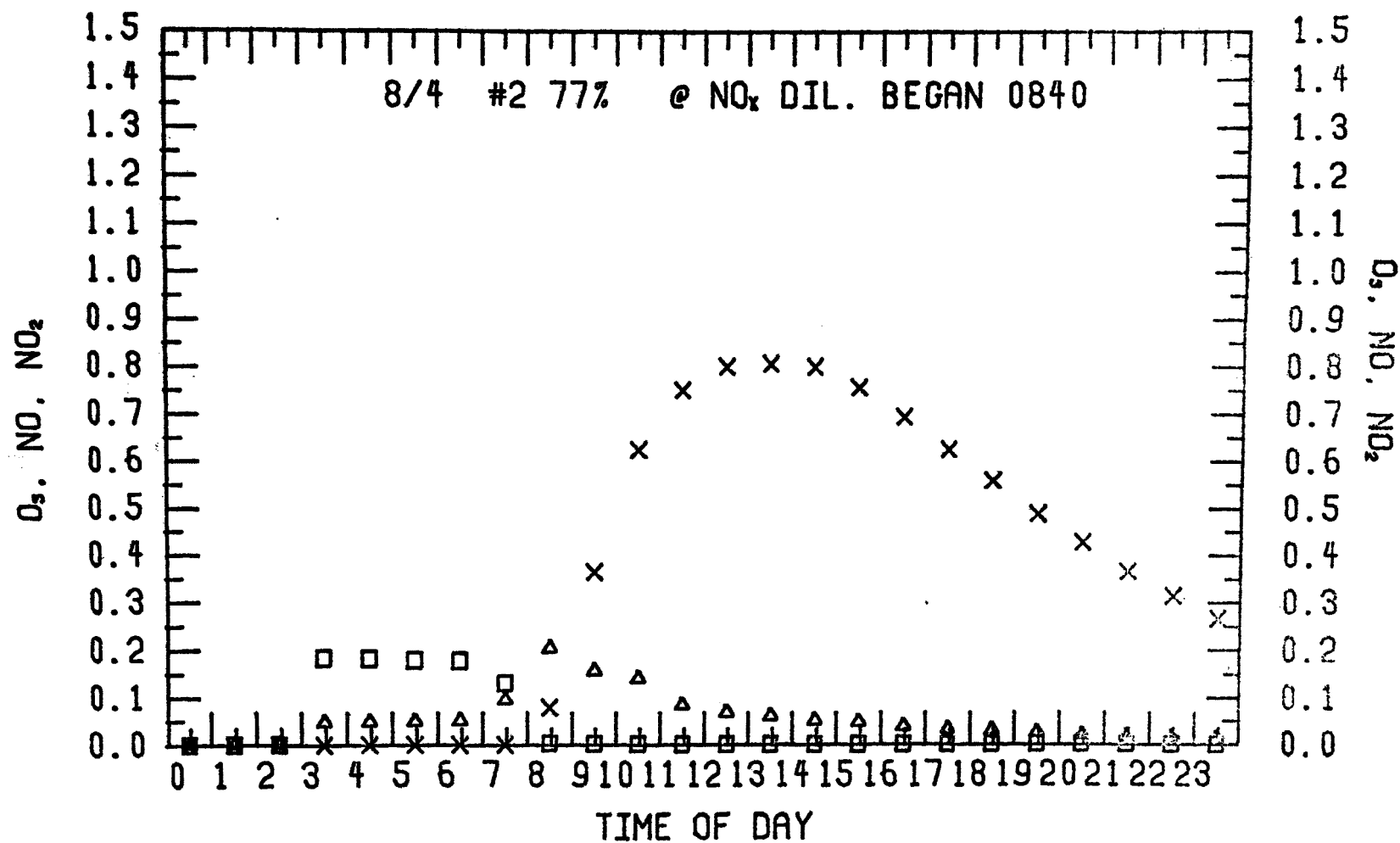


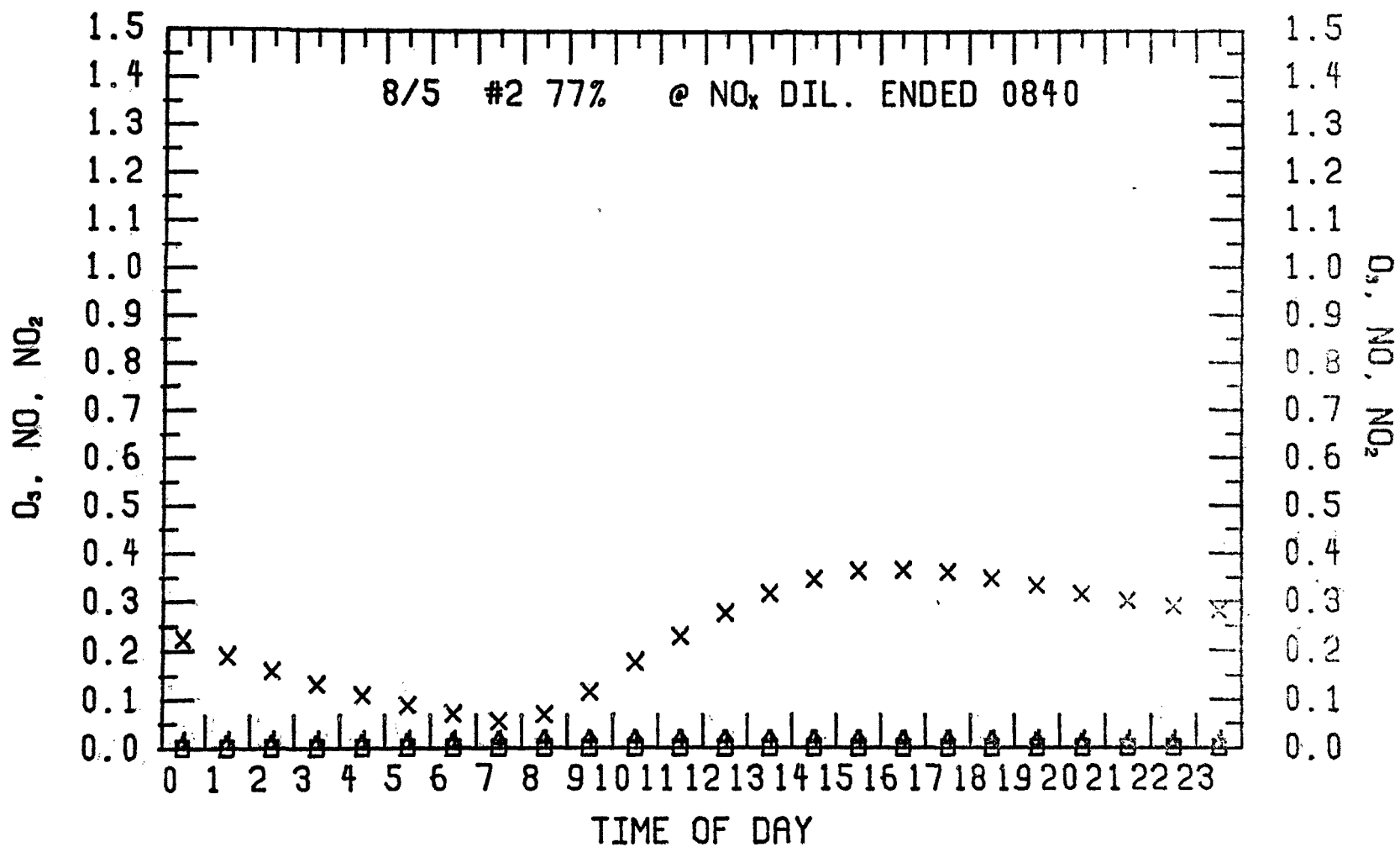


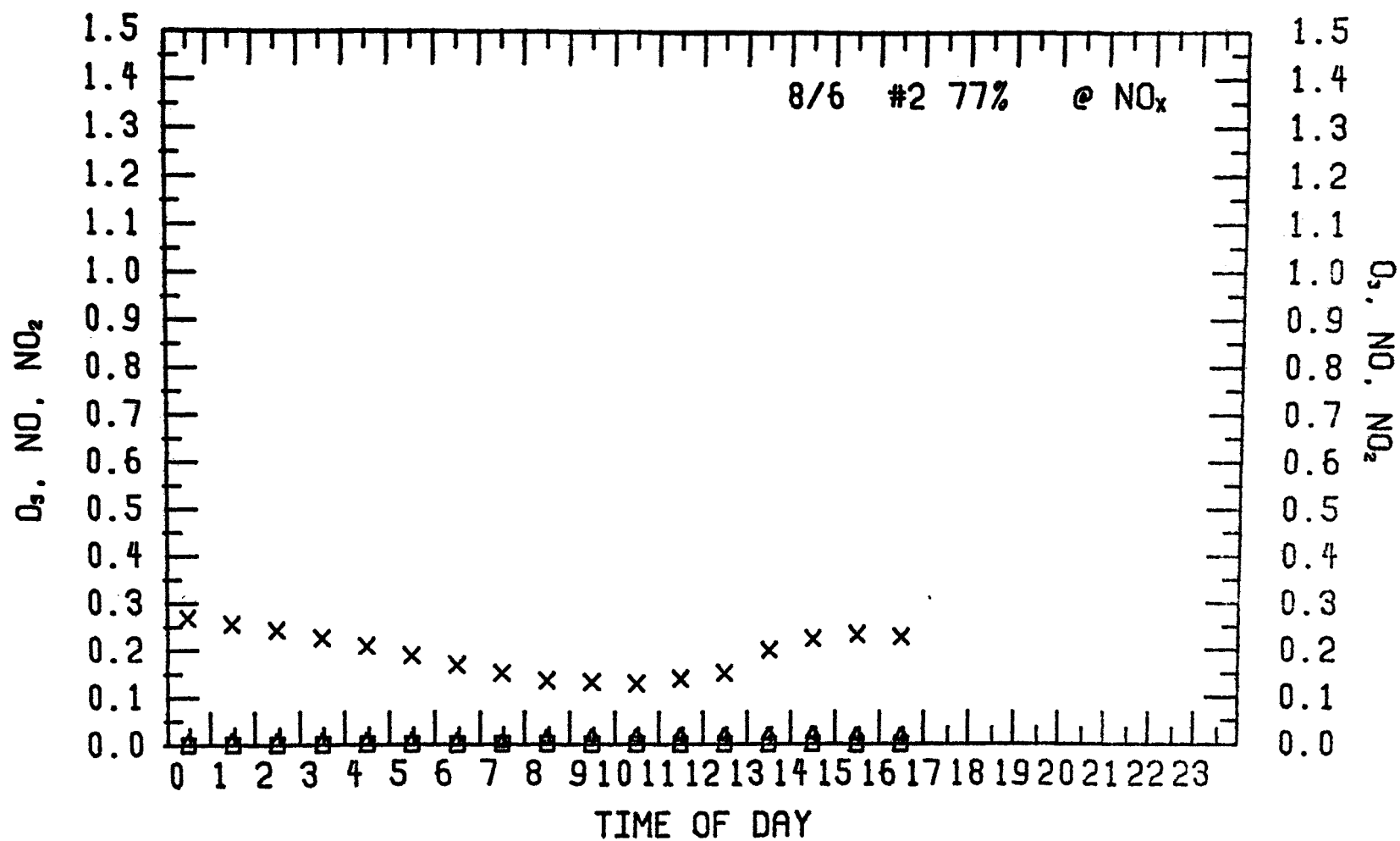




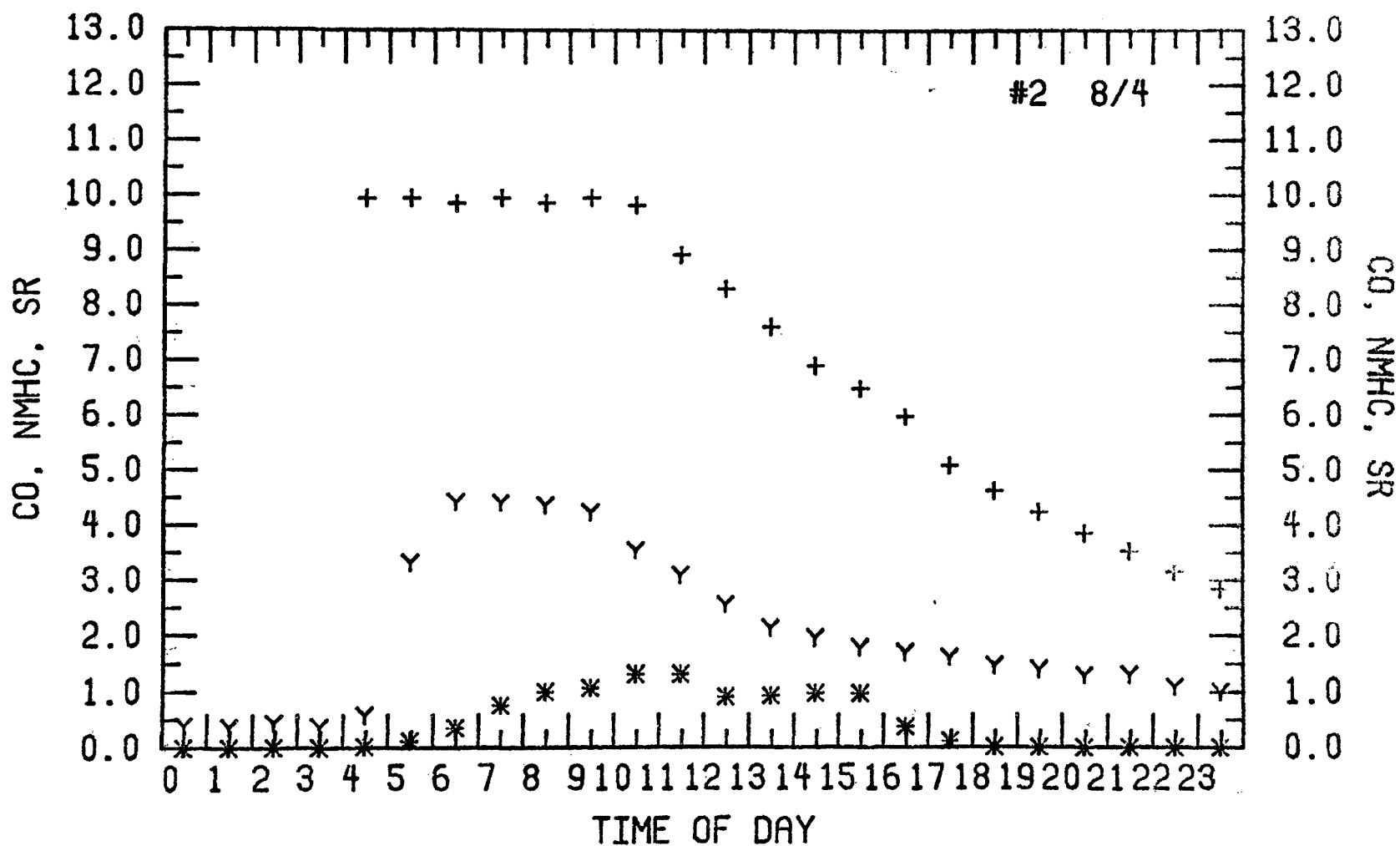


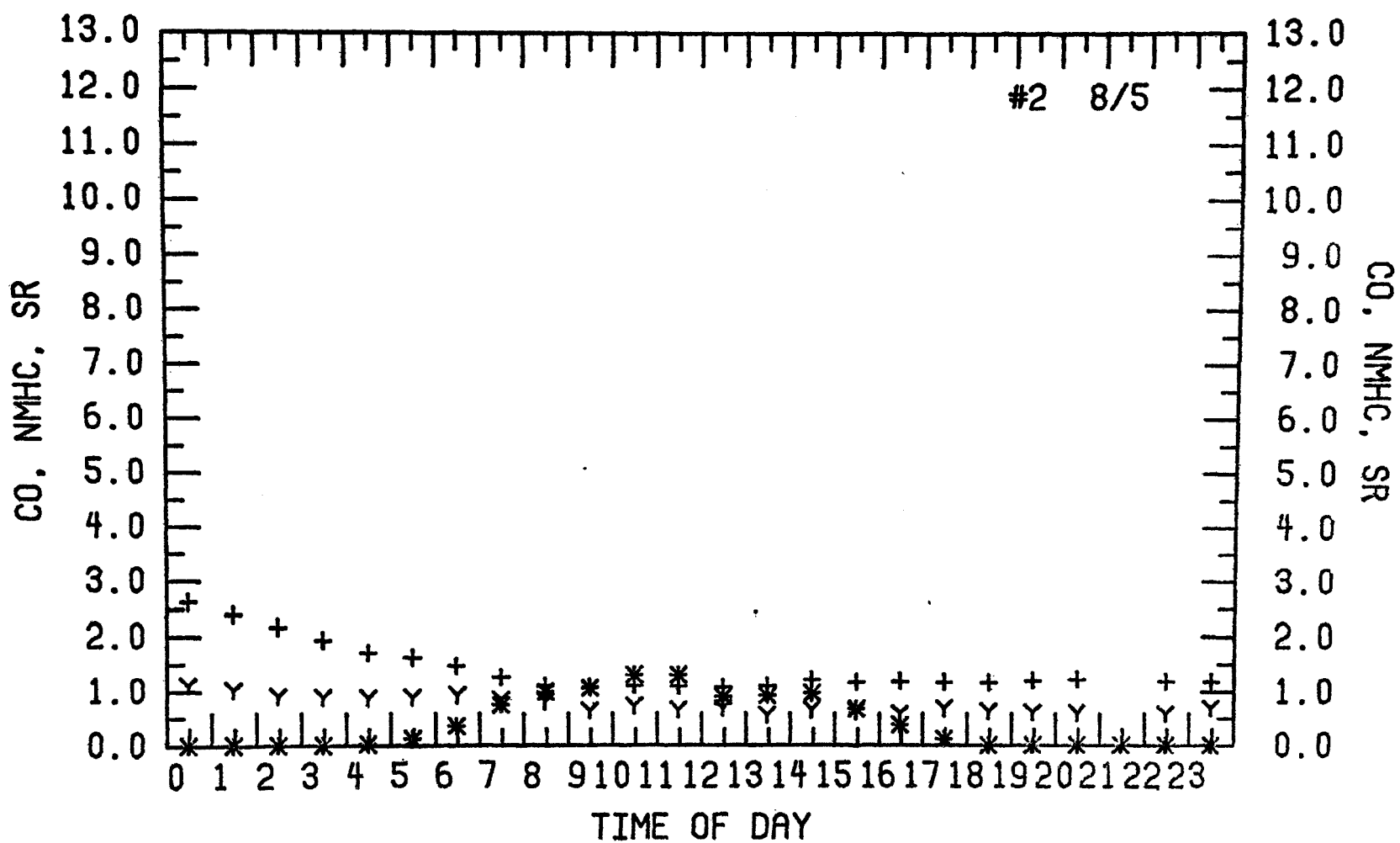


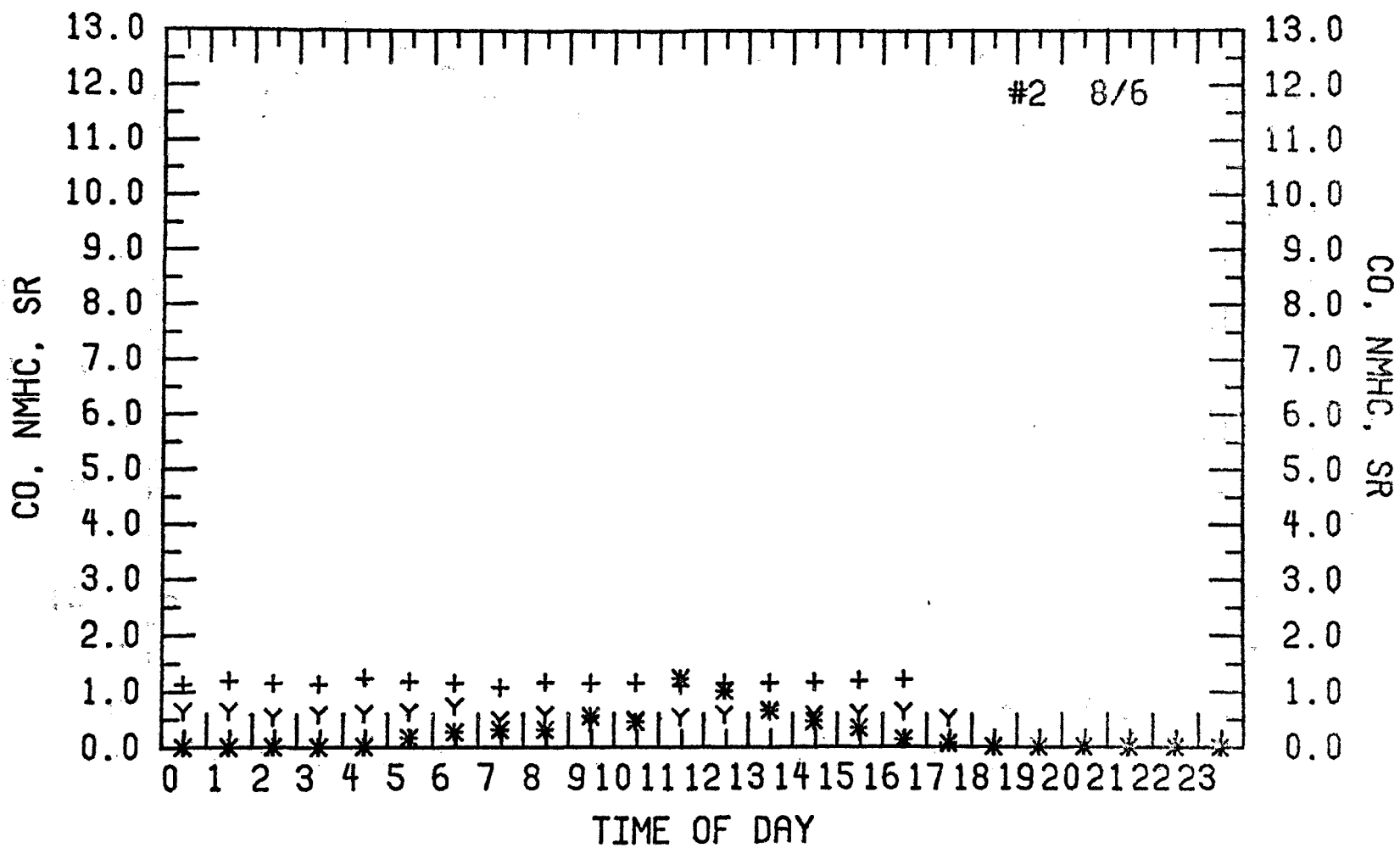


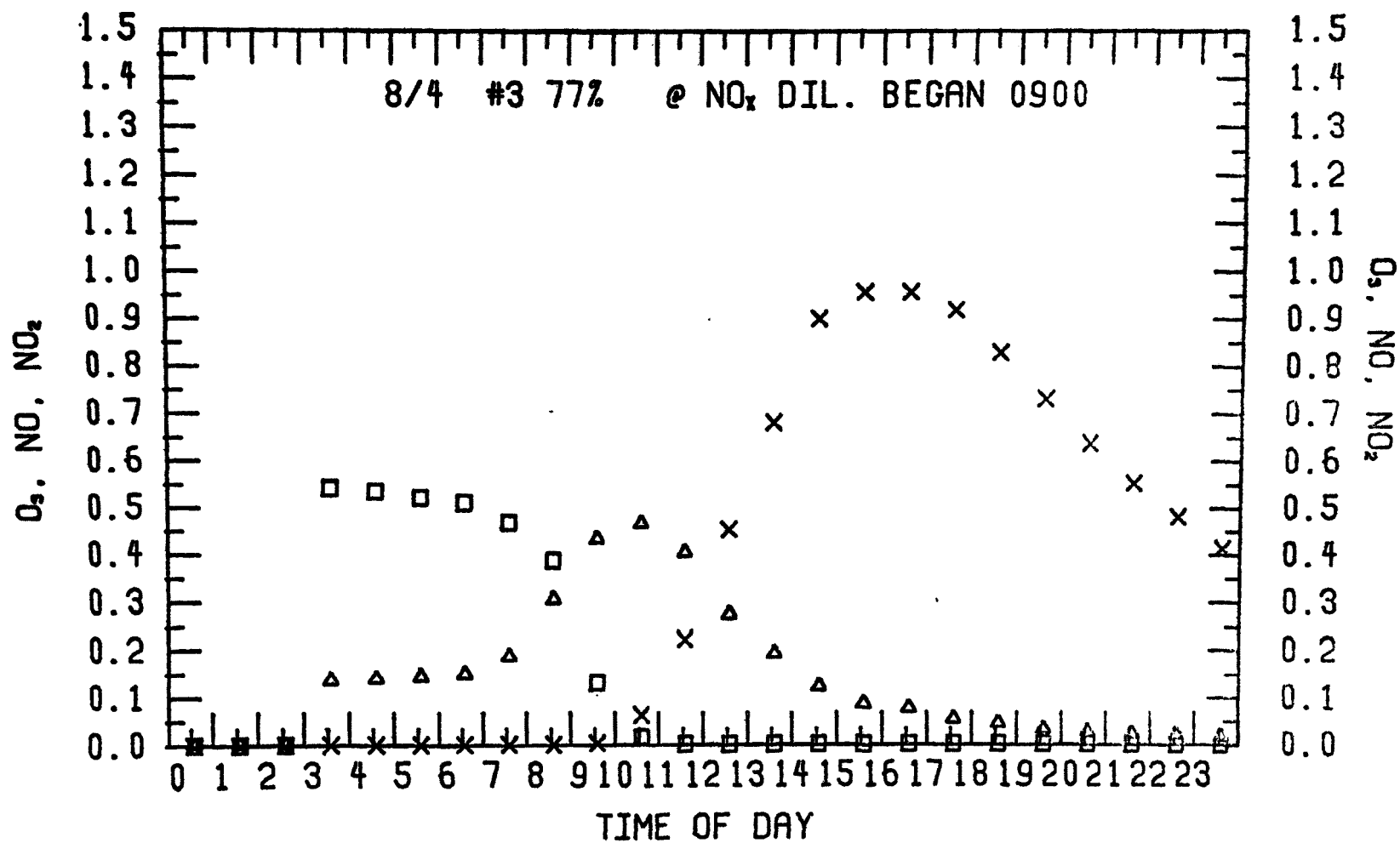


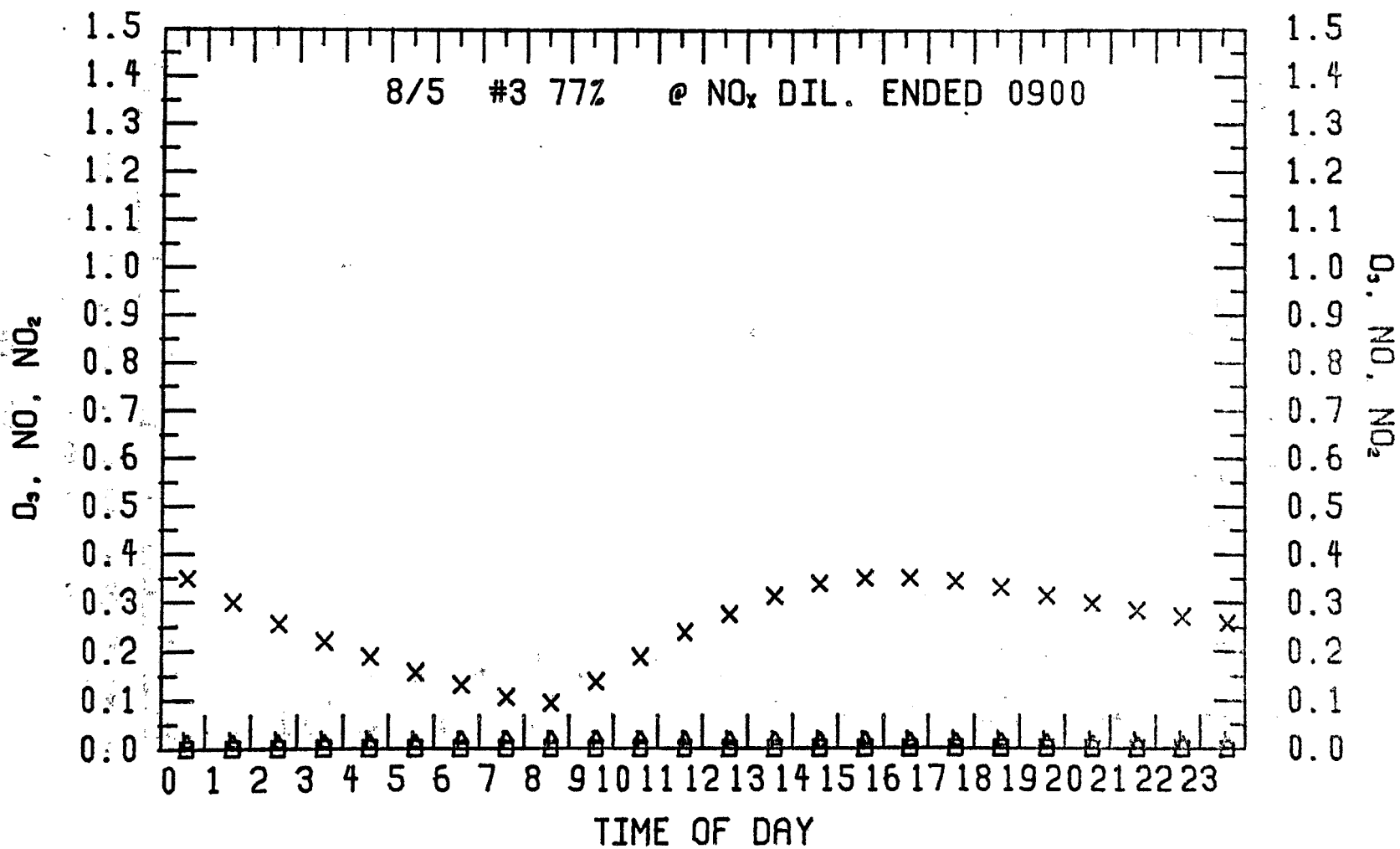


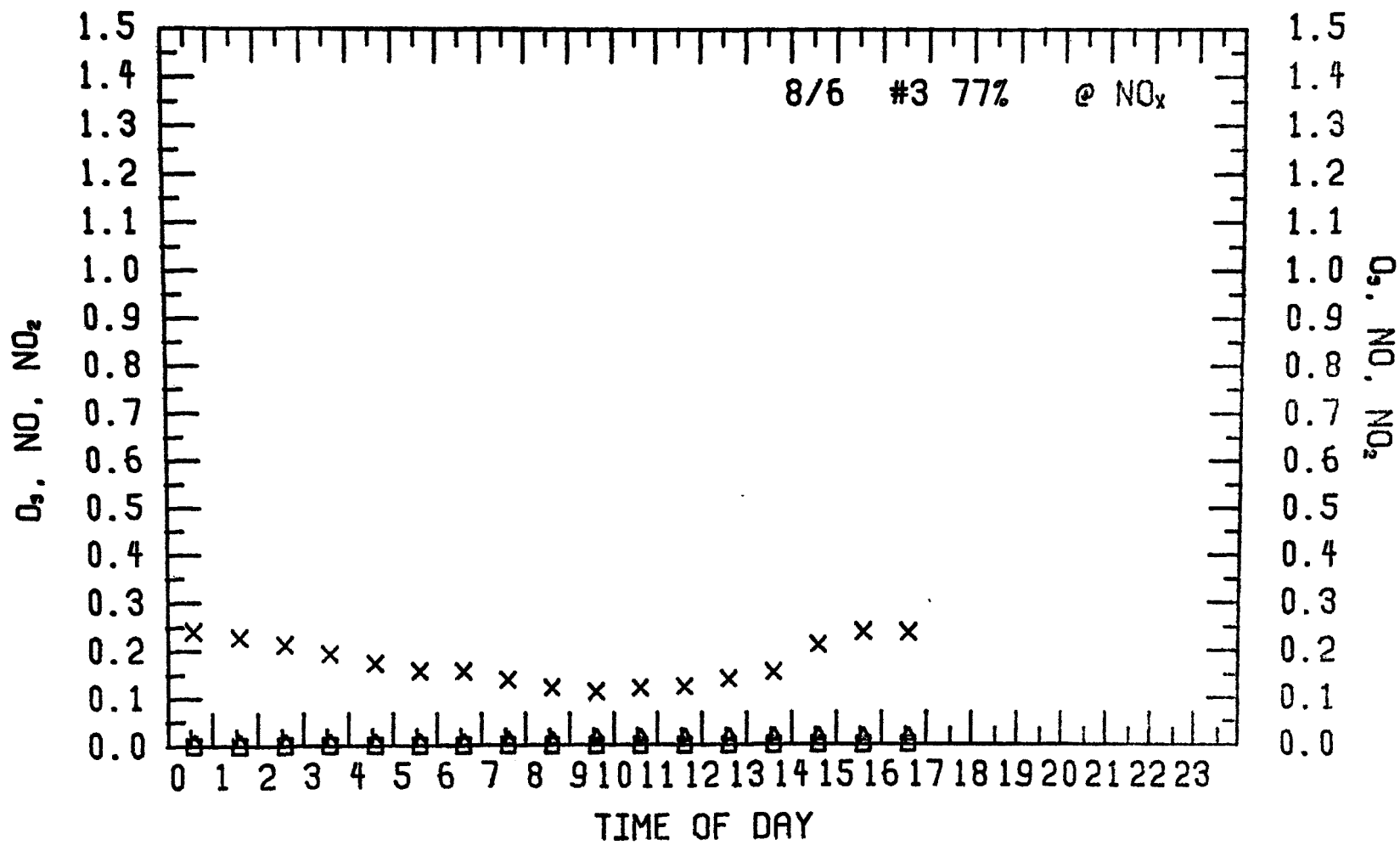


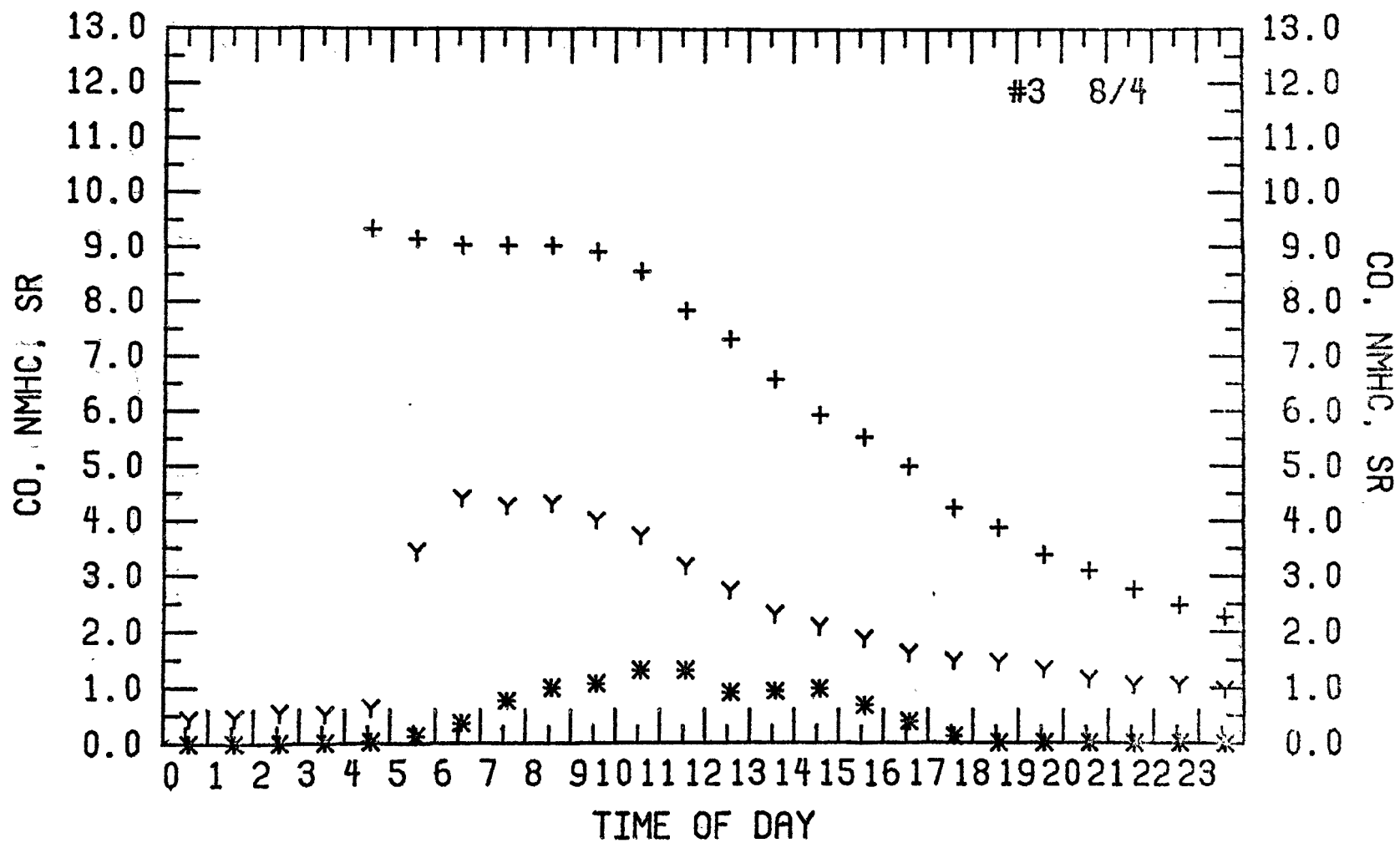


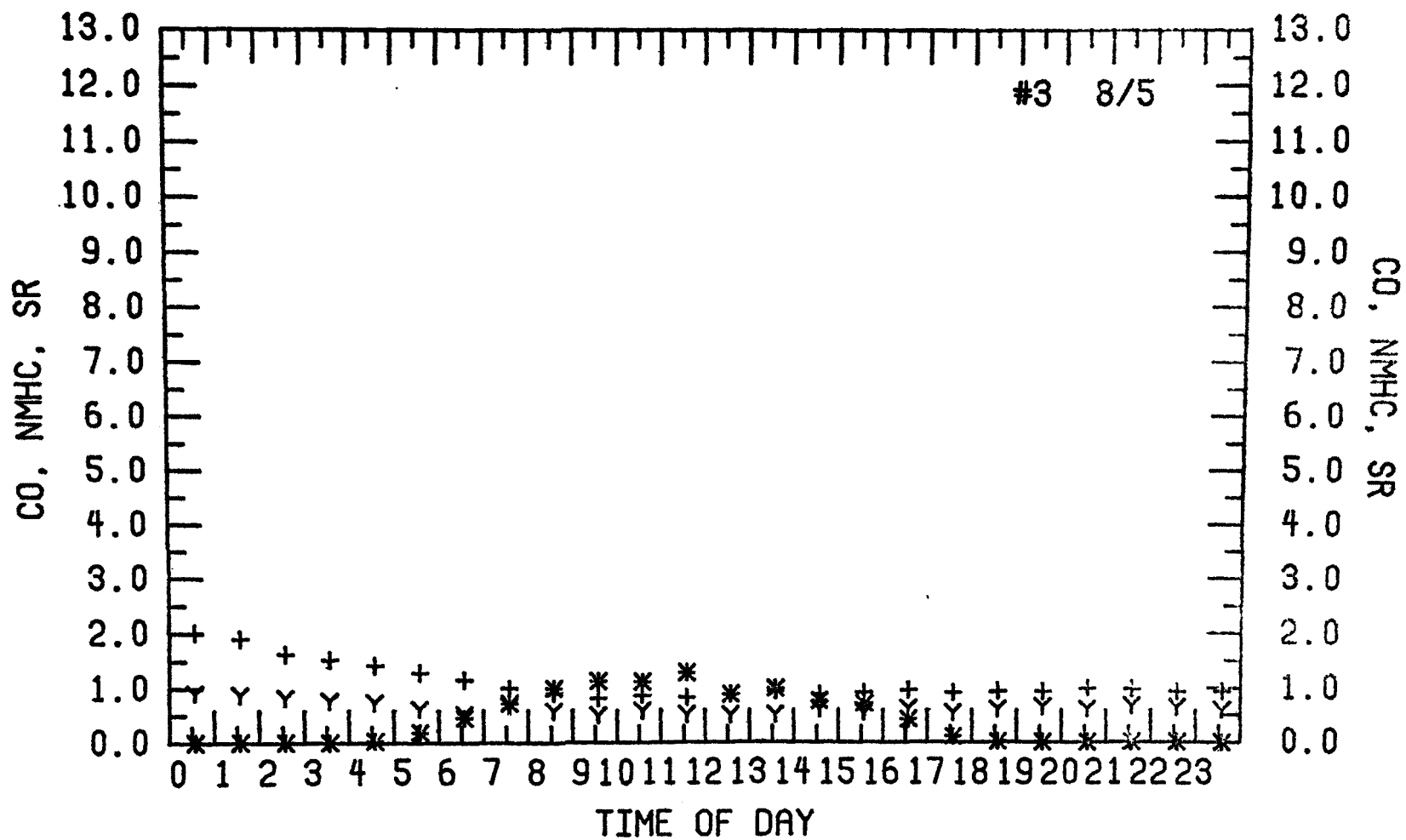




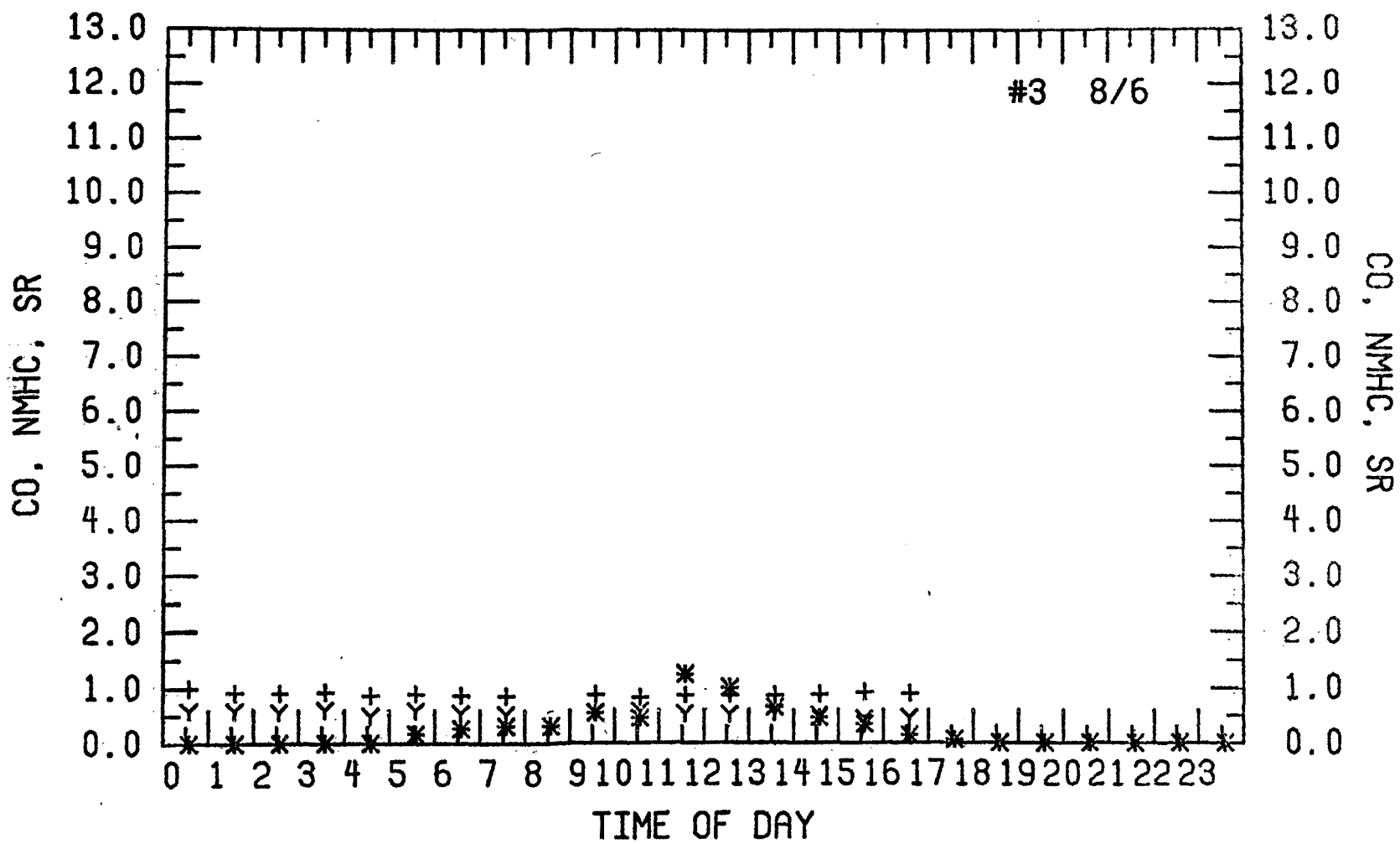


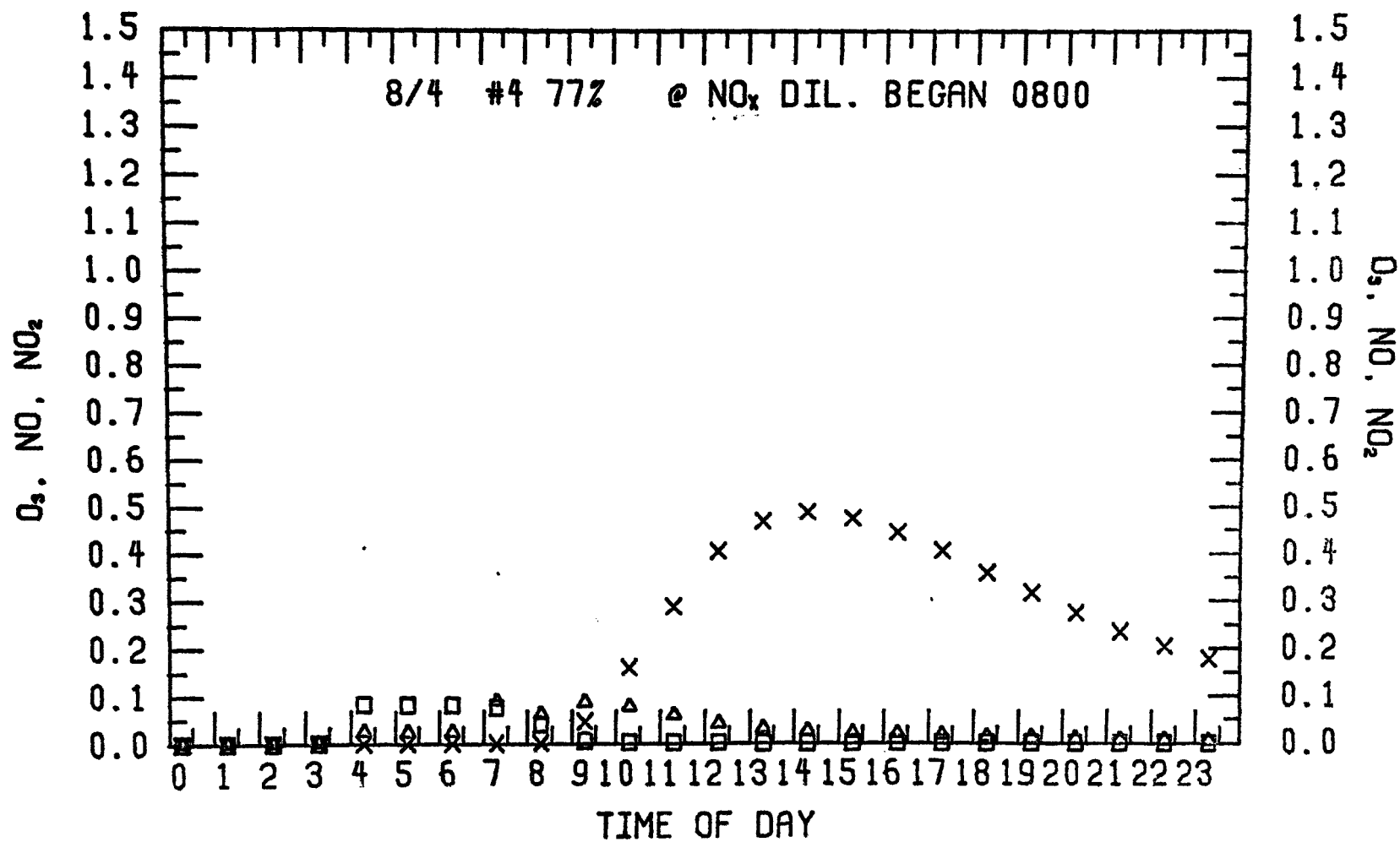


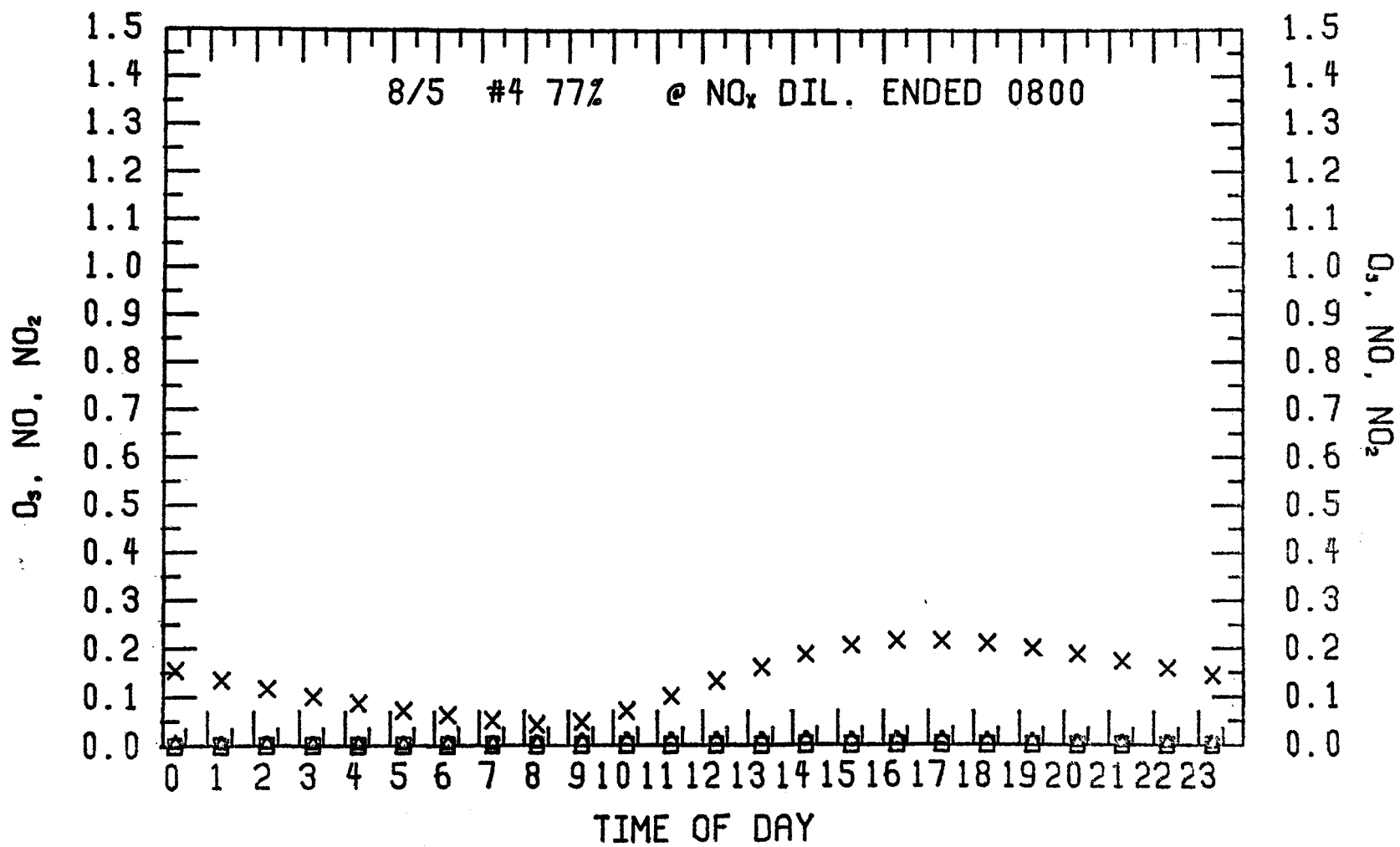


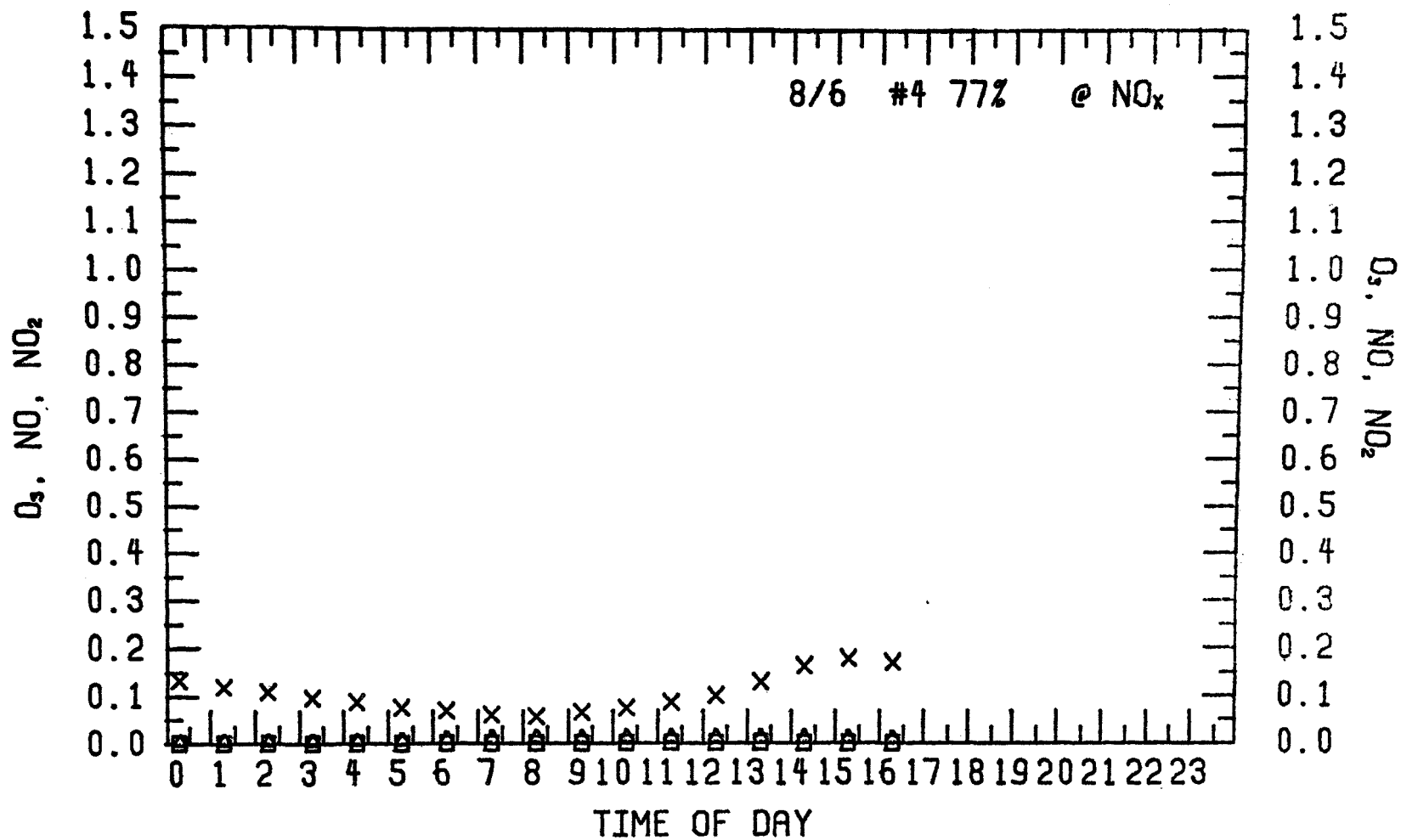


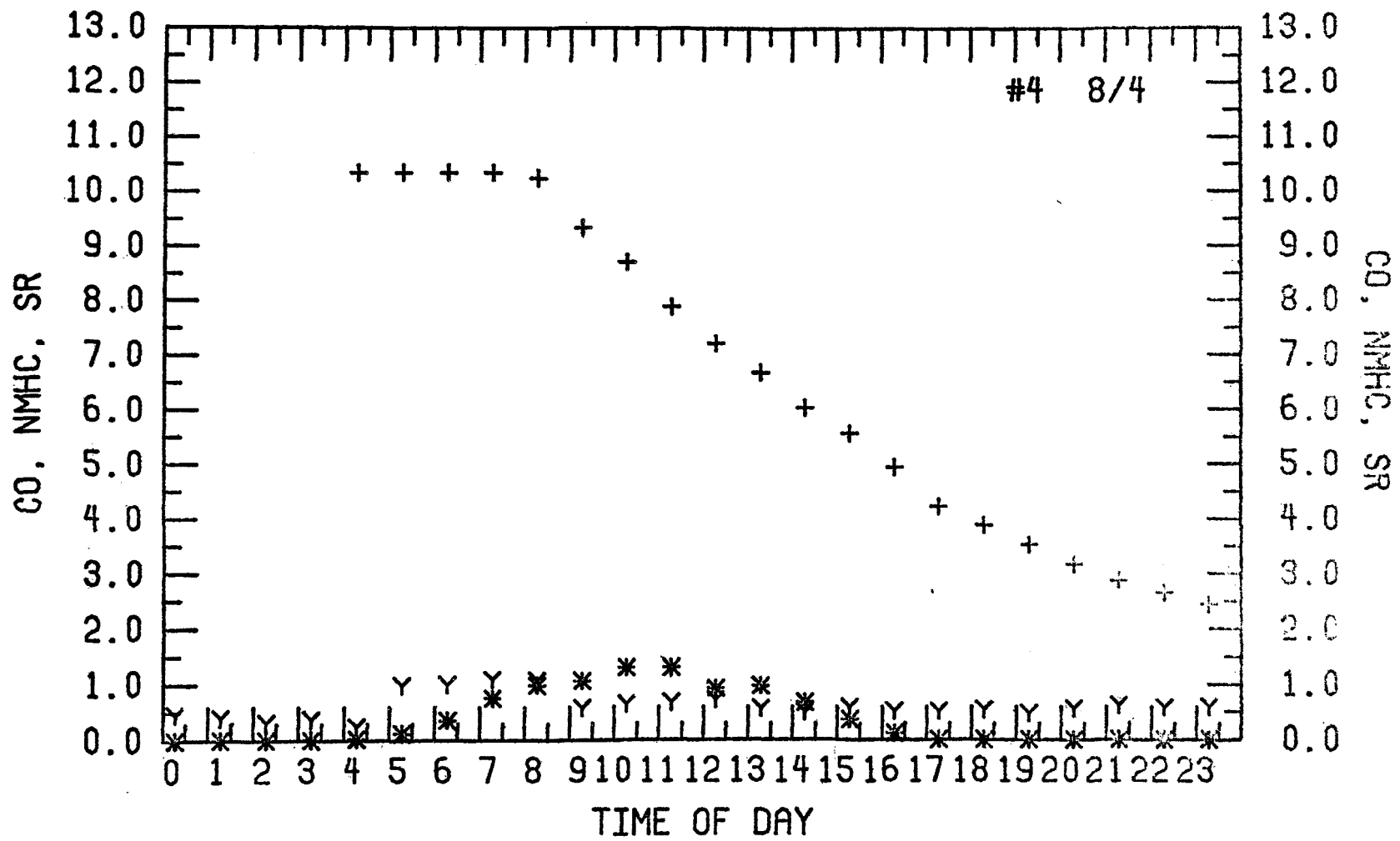


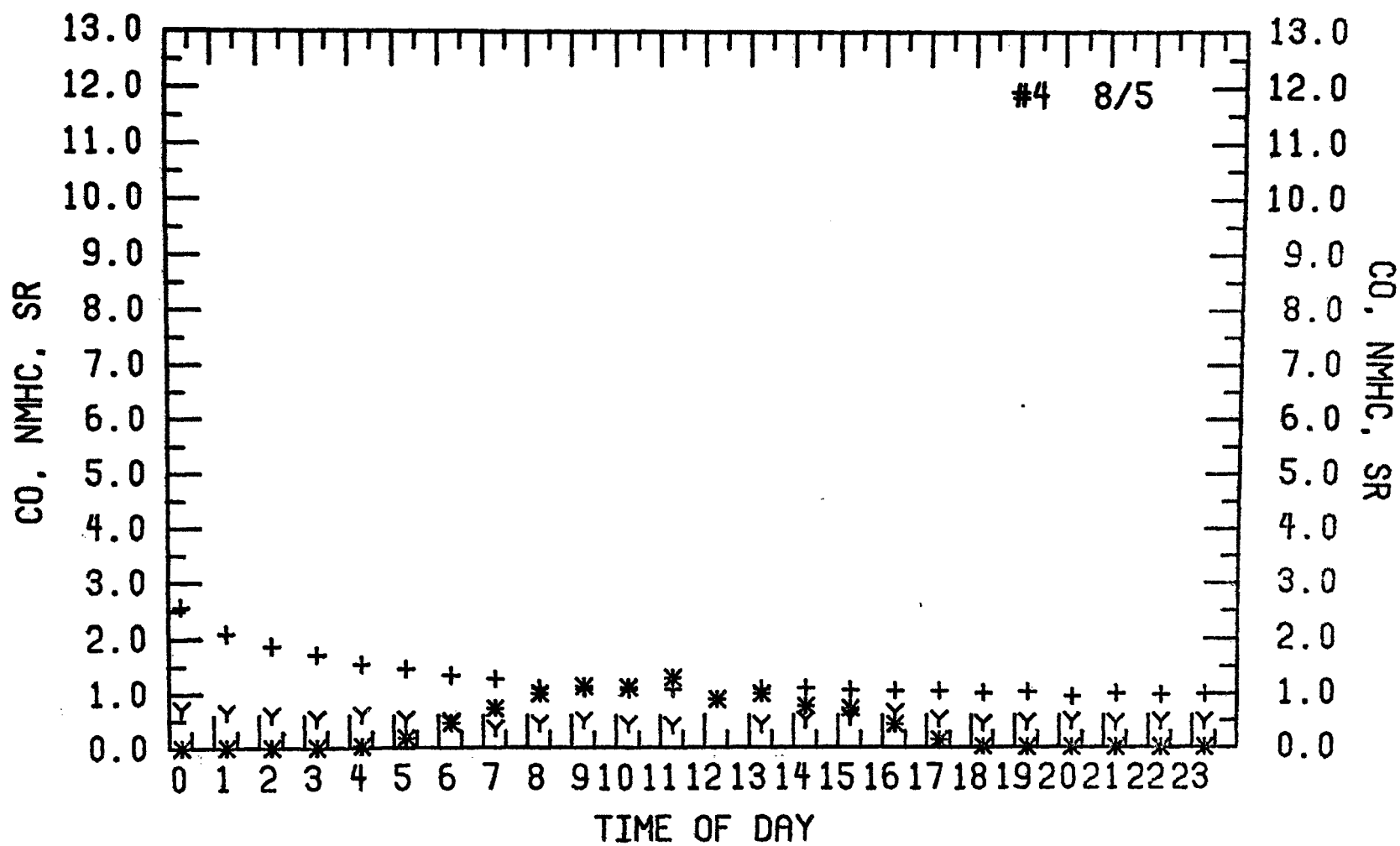


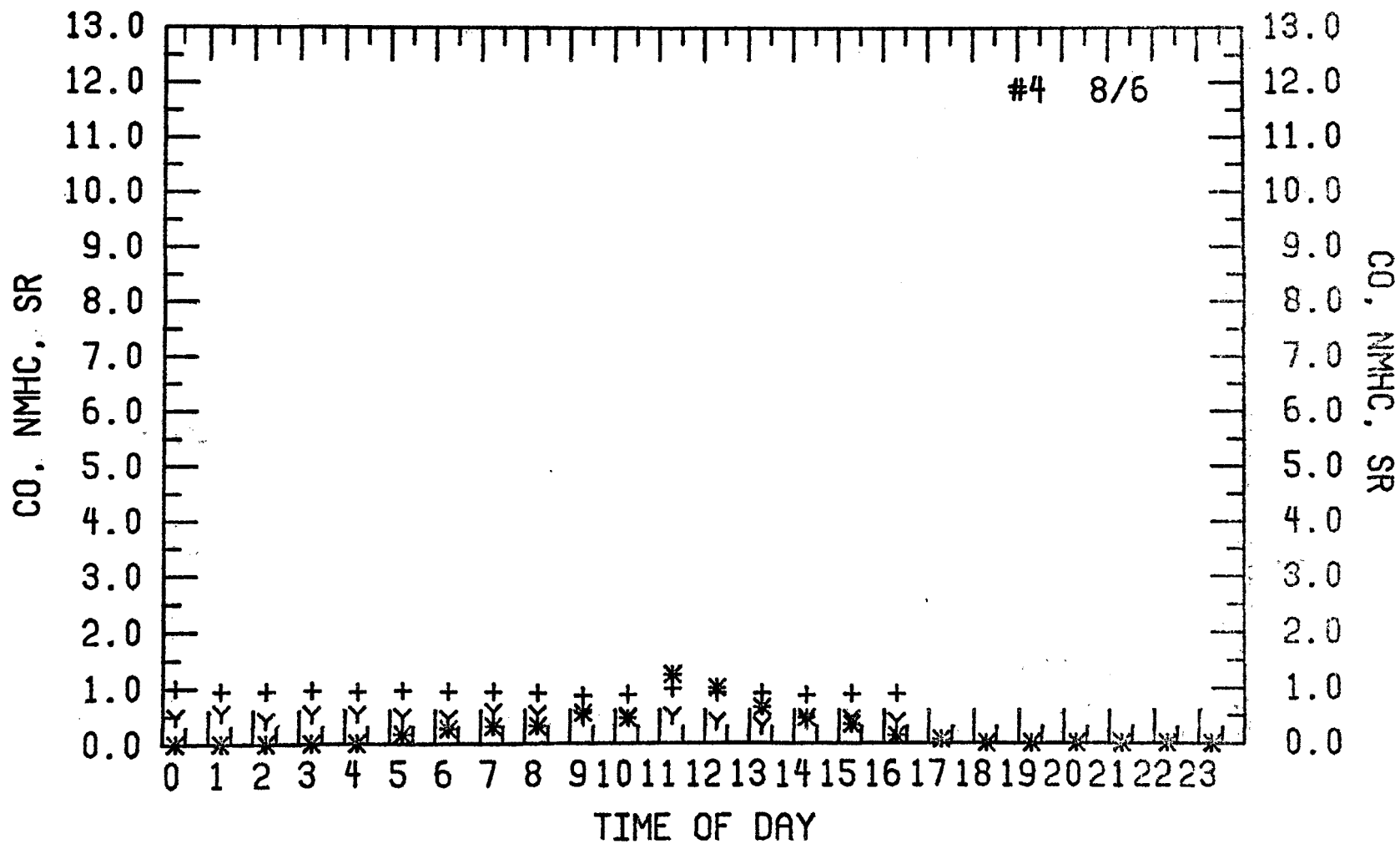


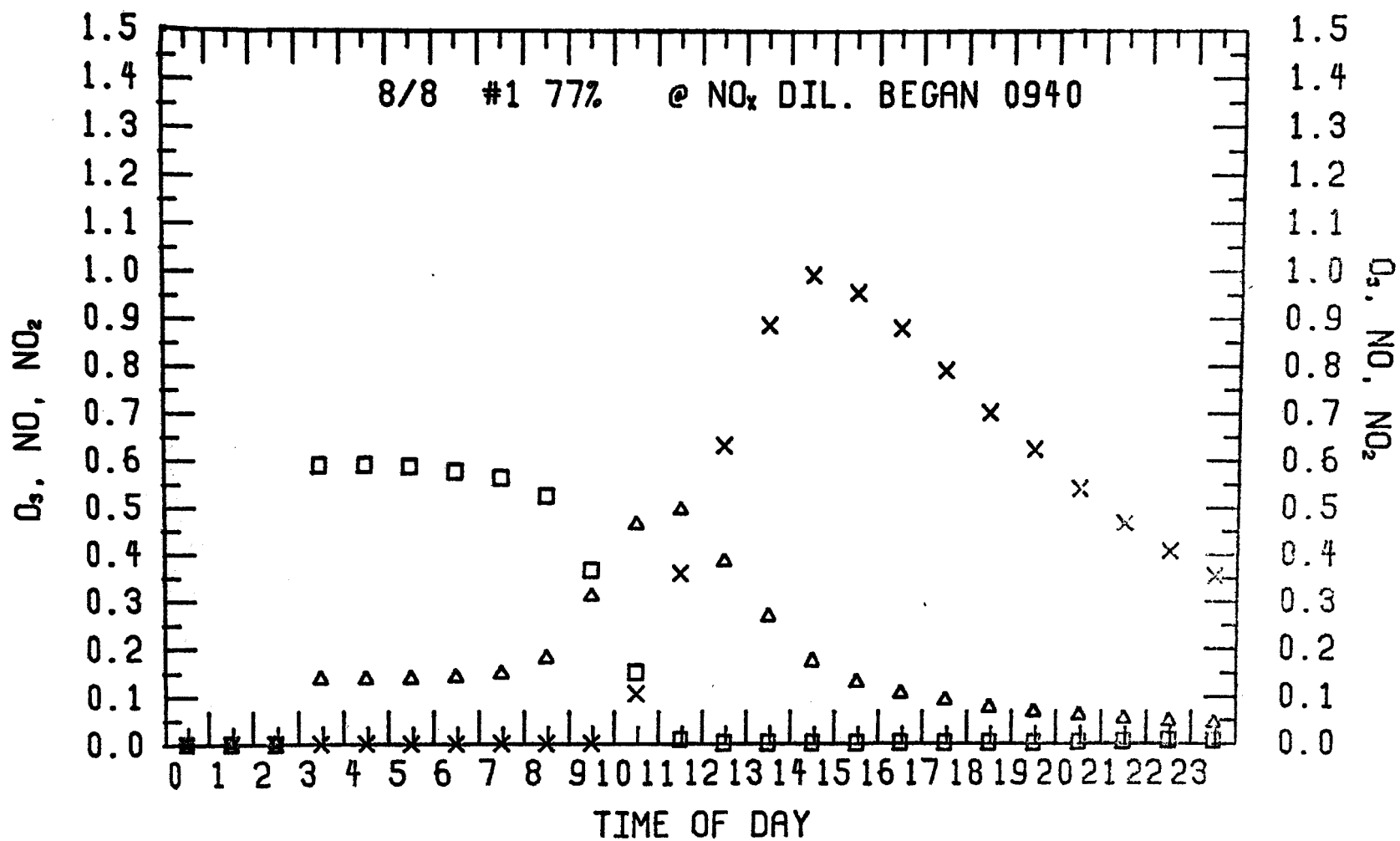




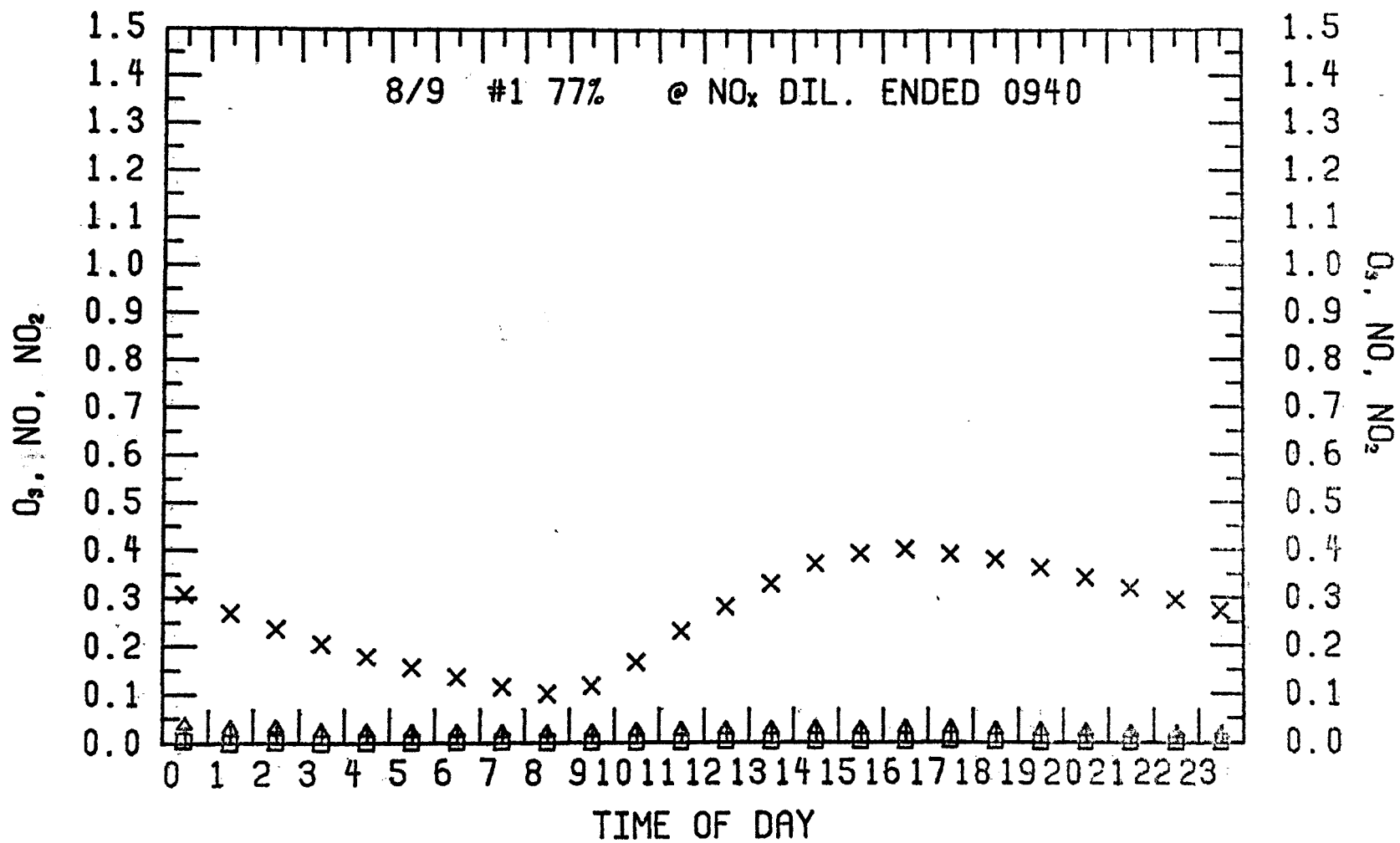


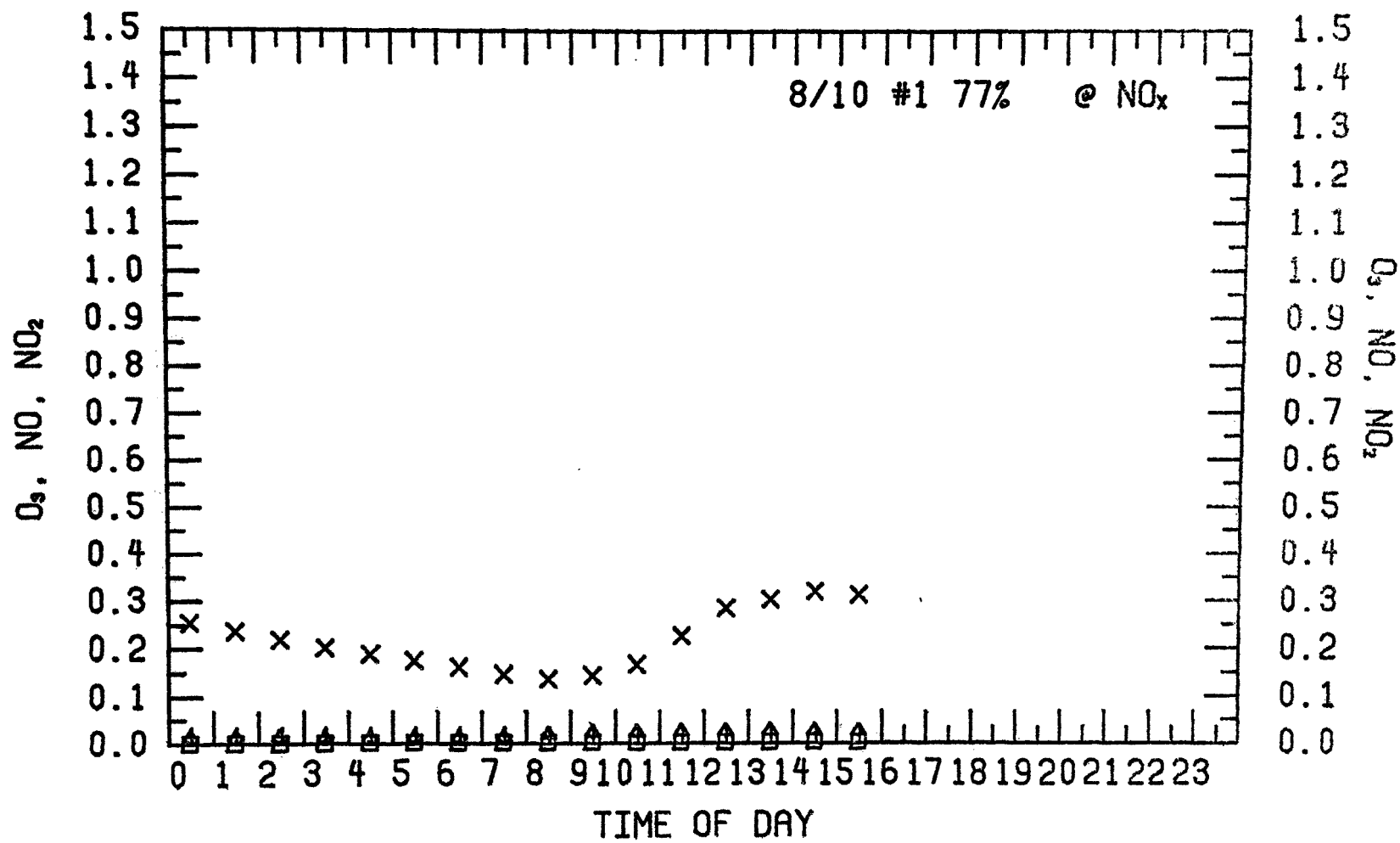


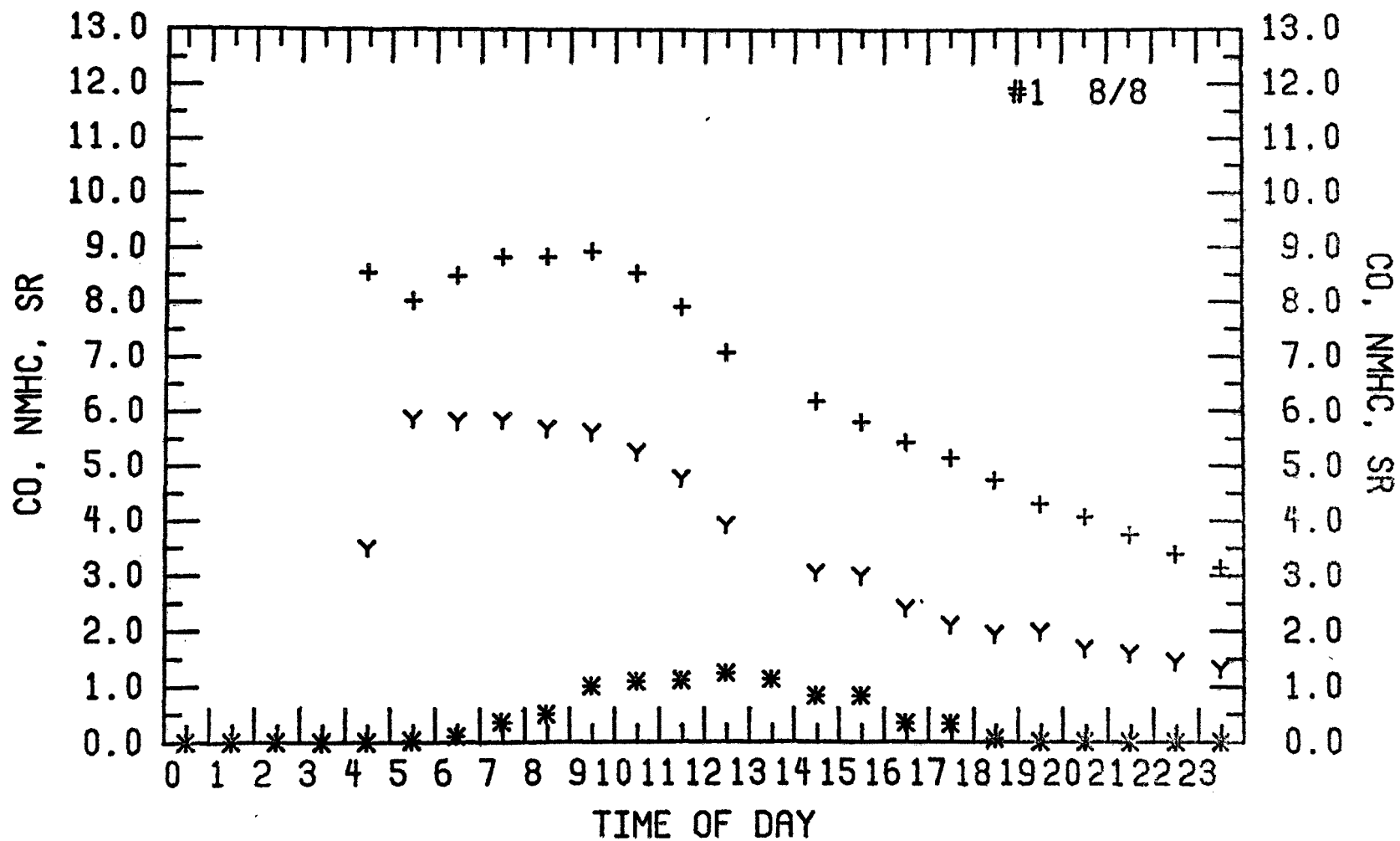


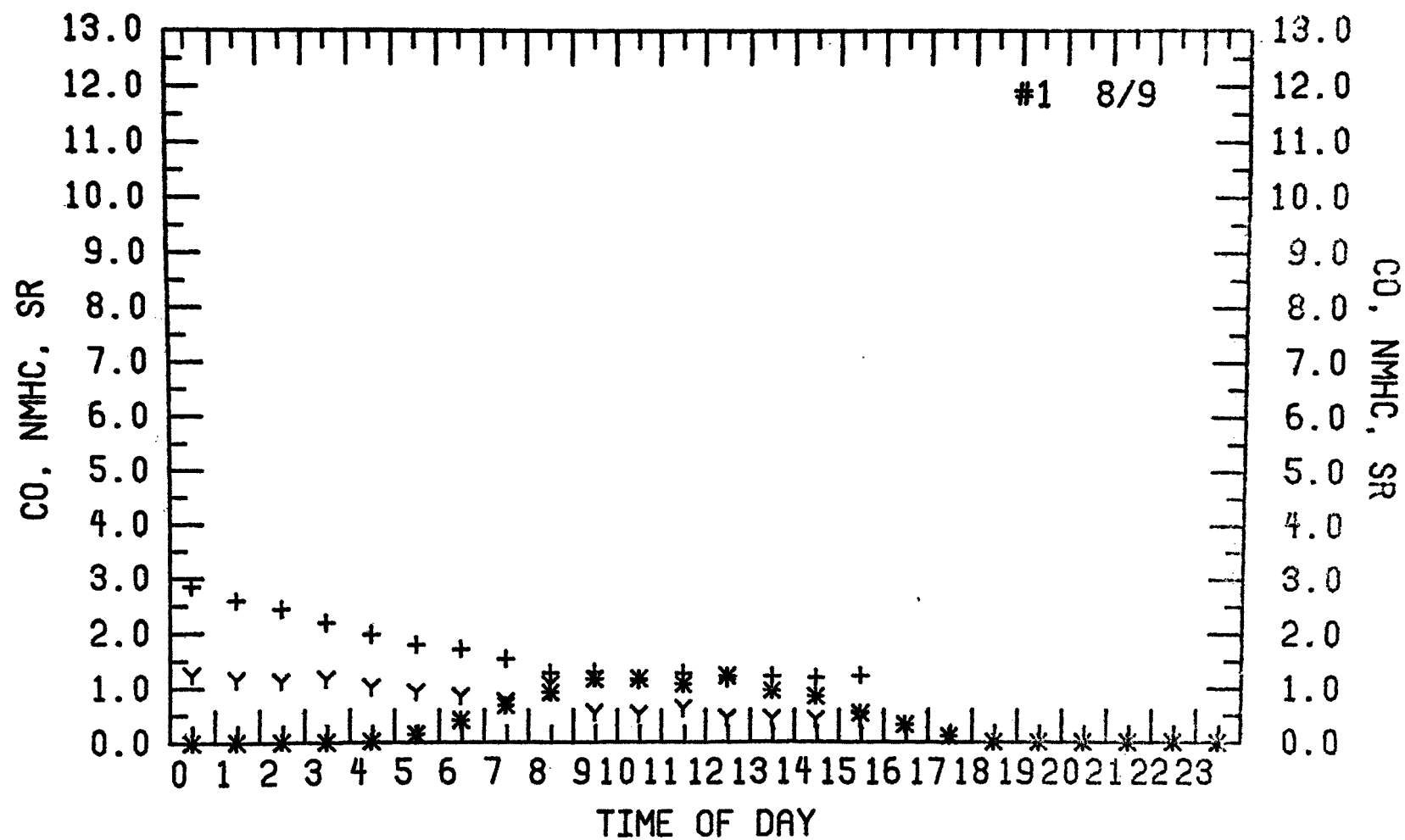


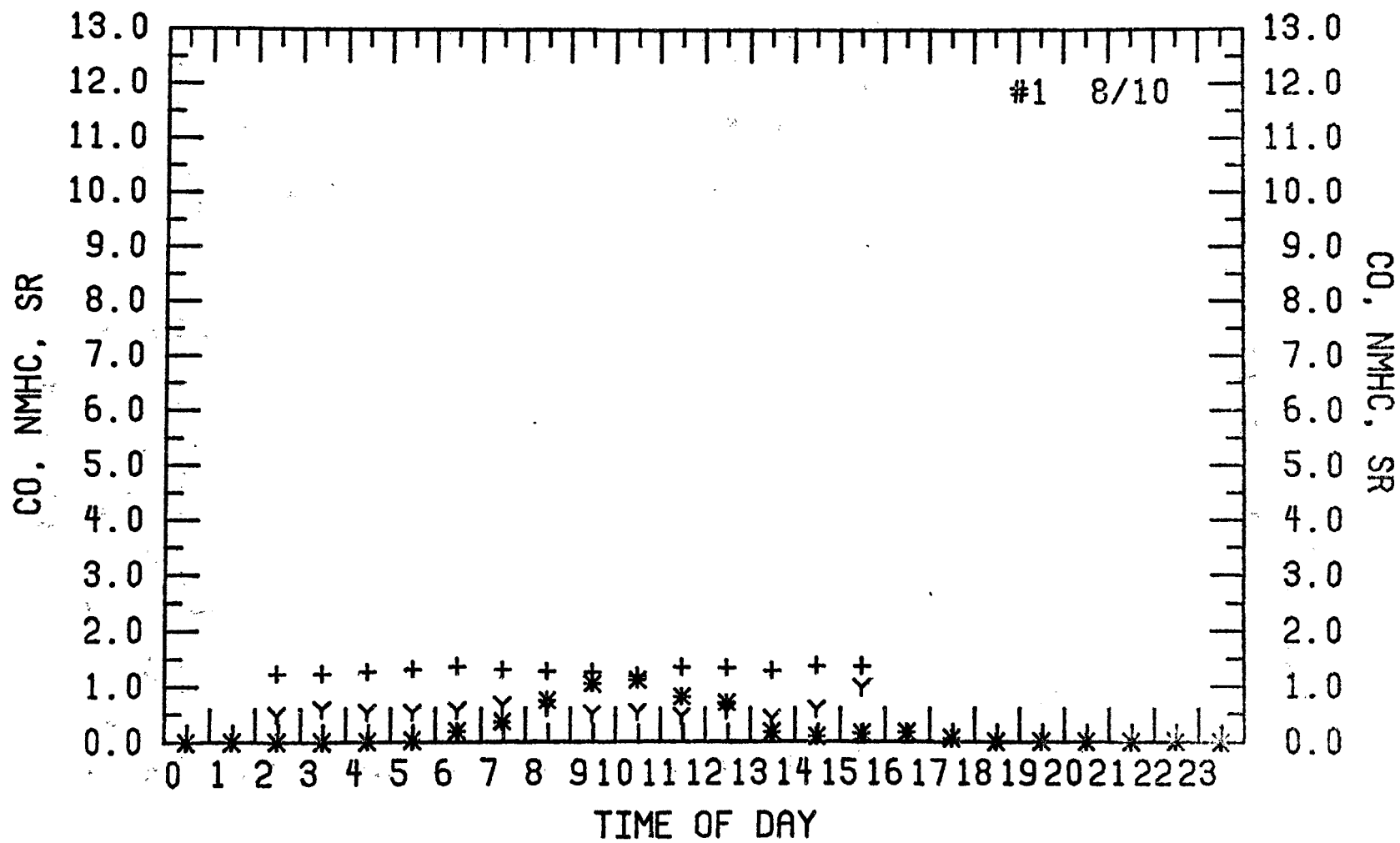




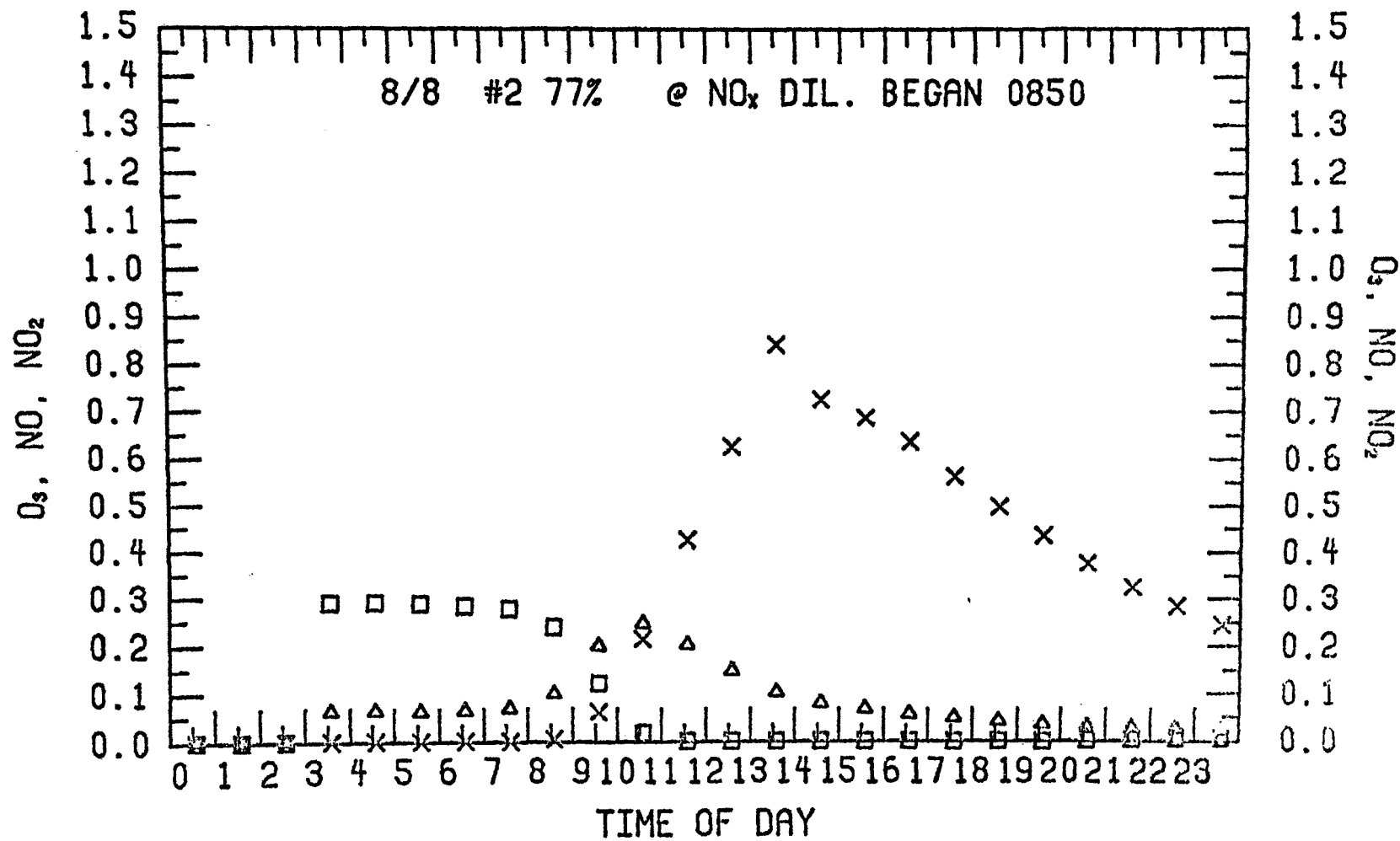


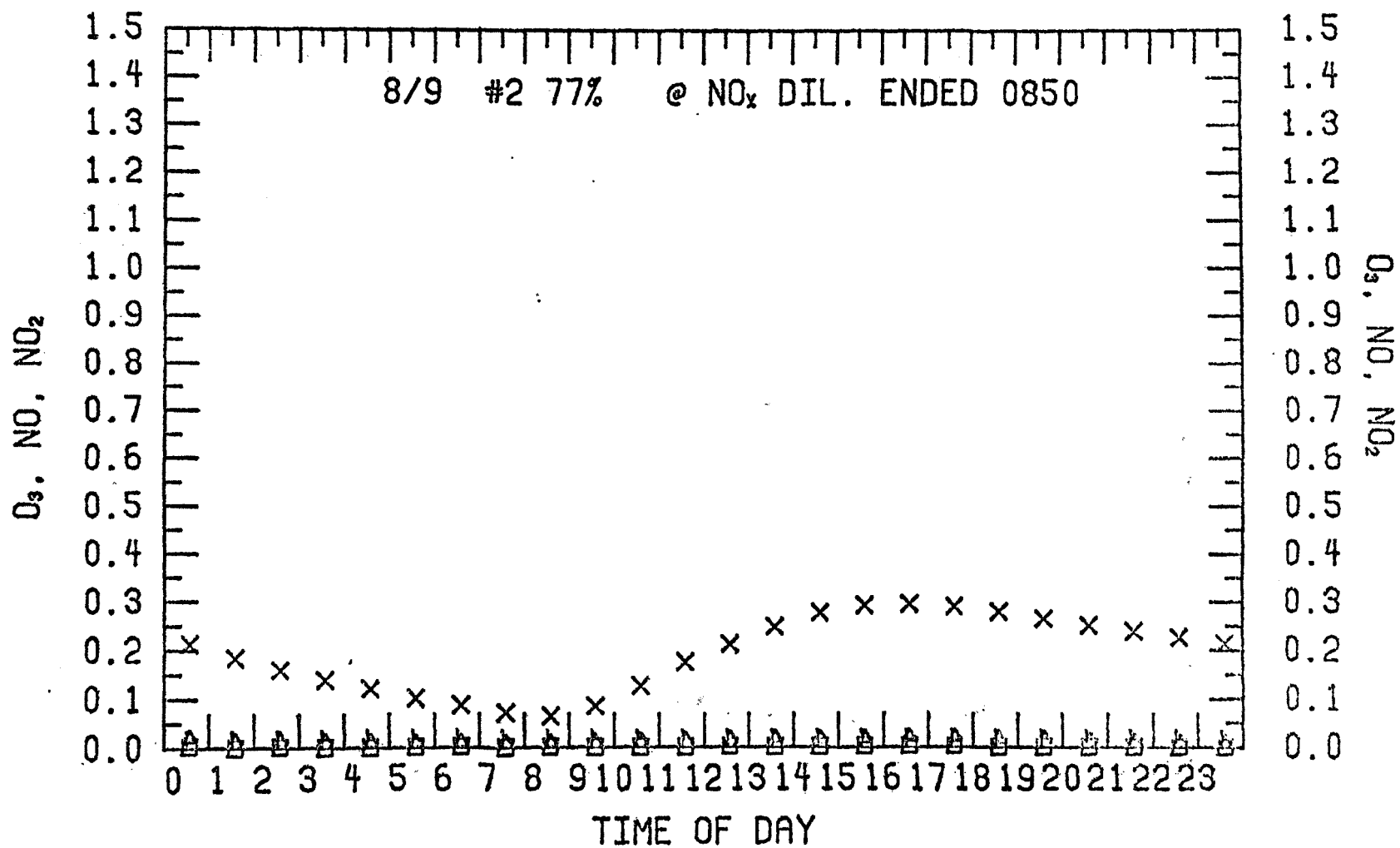


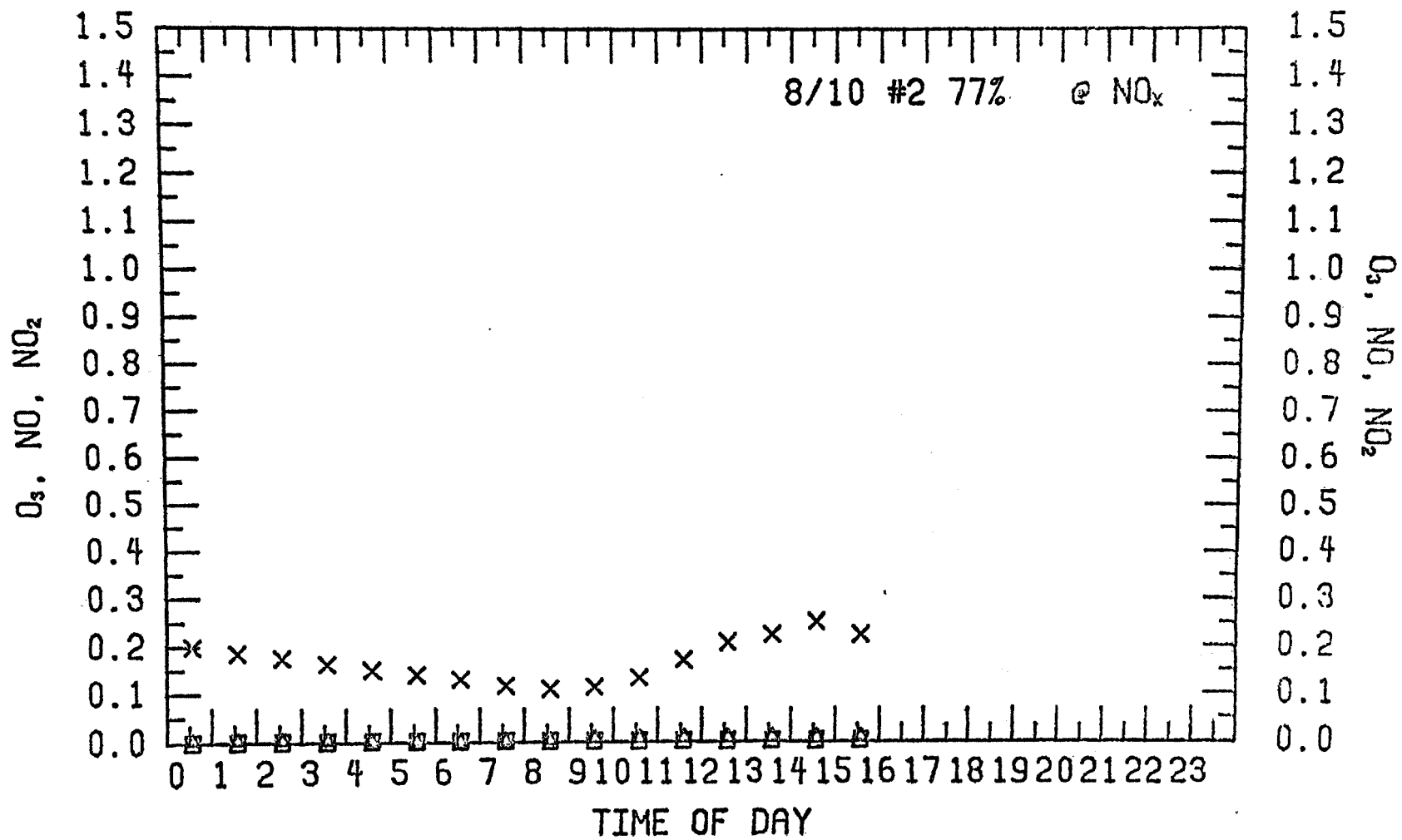




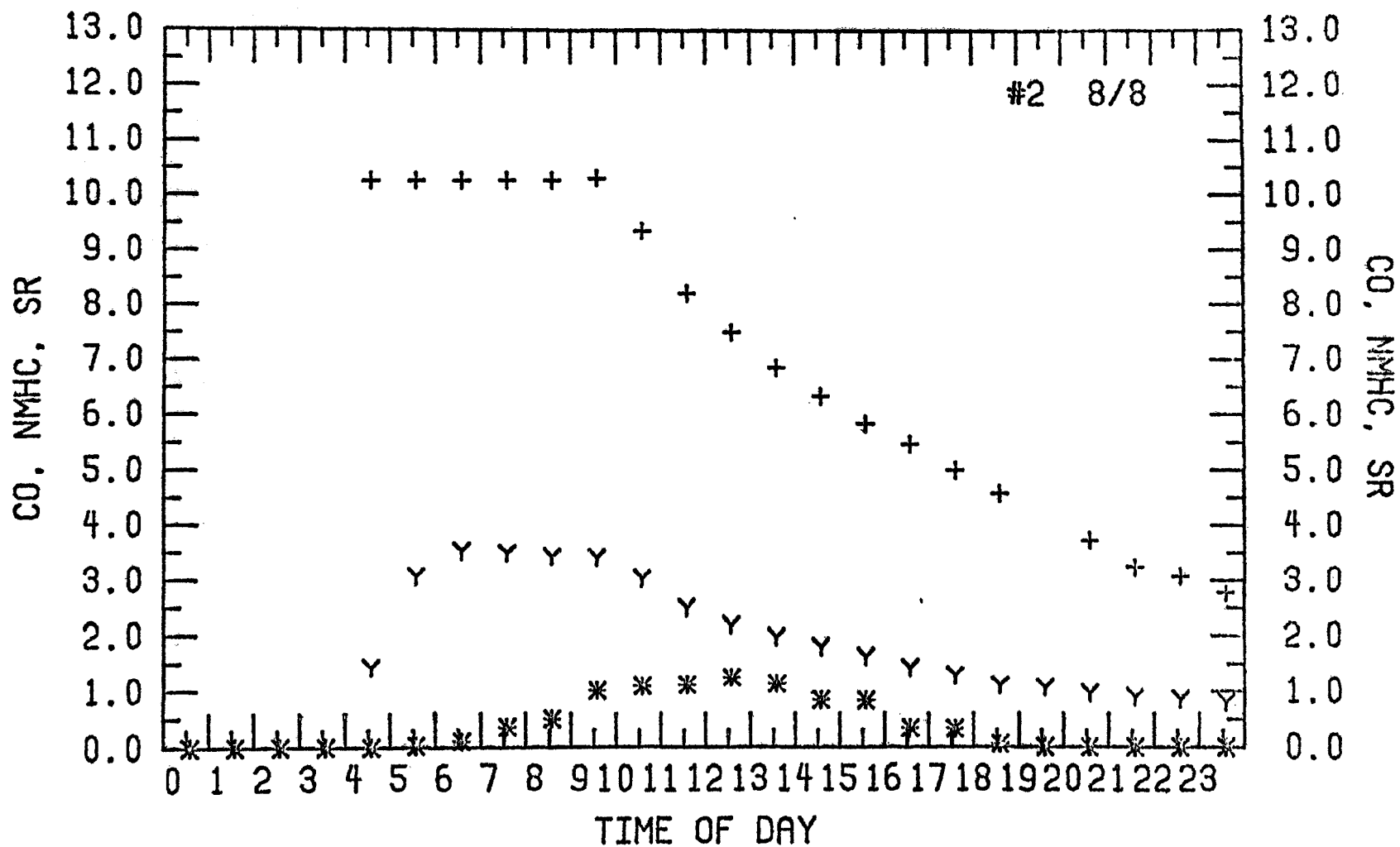
173

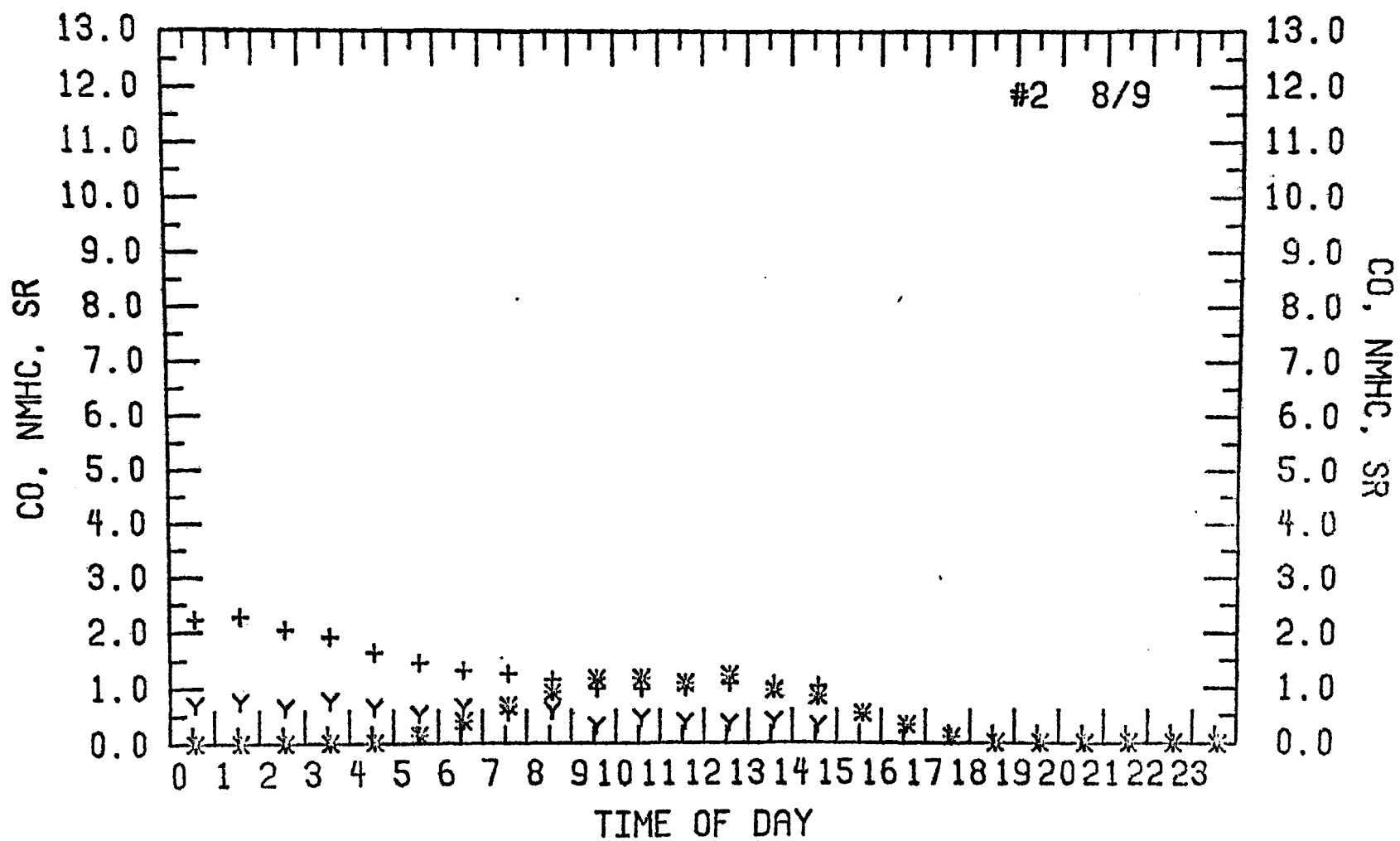


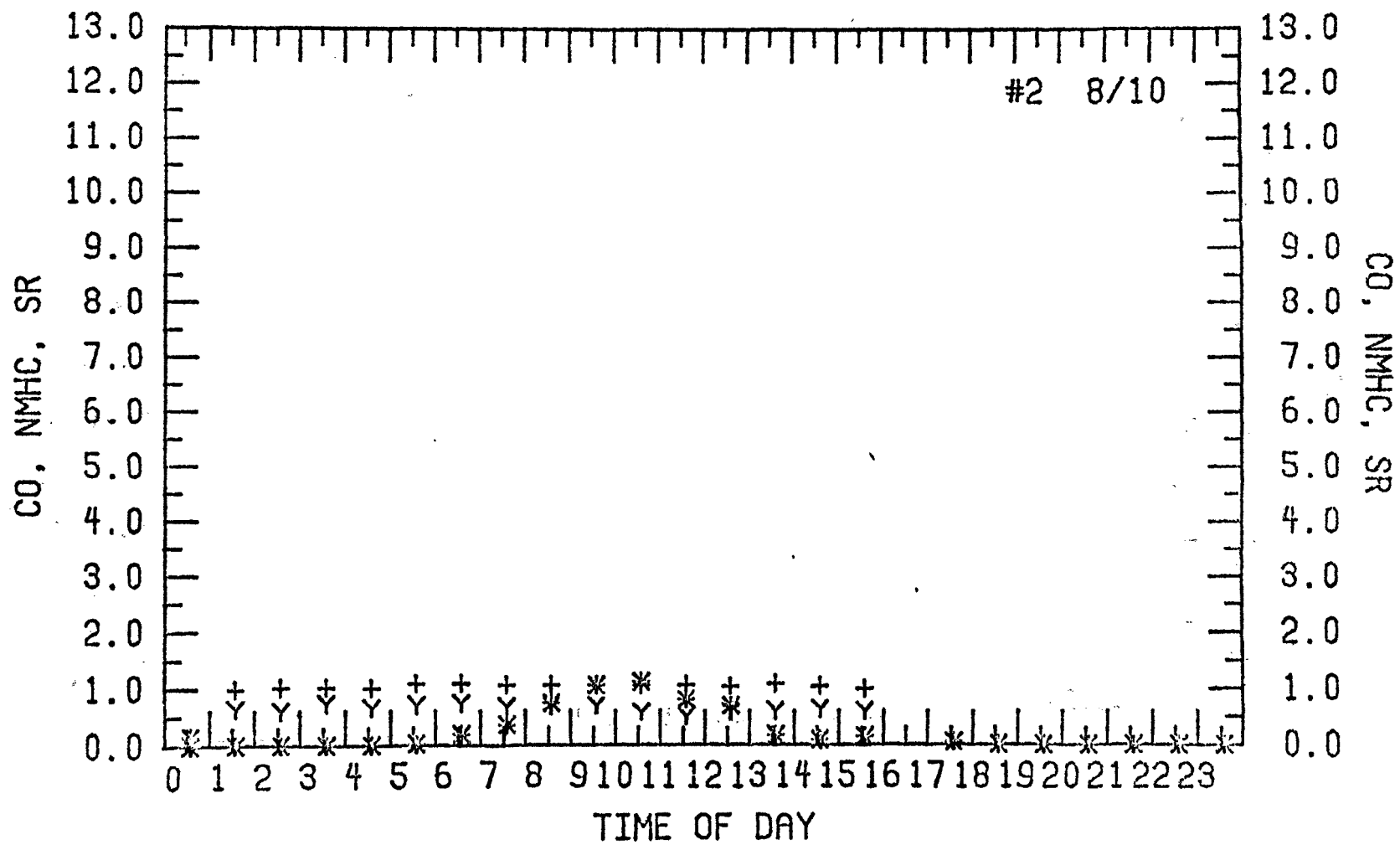


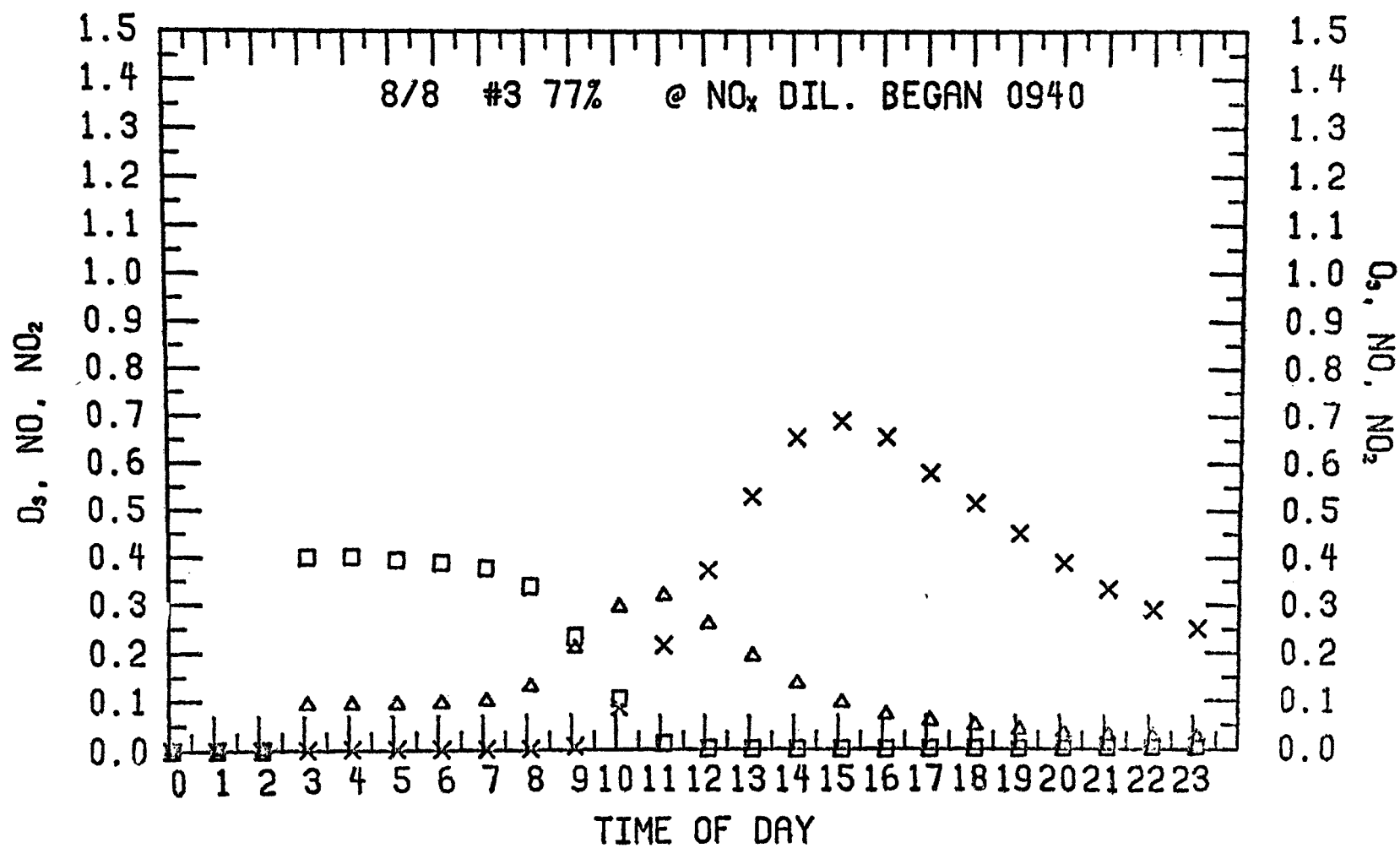


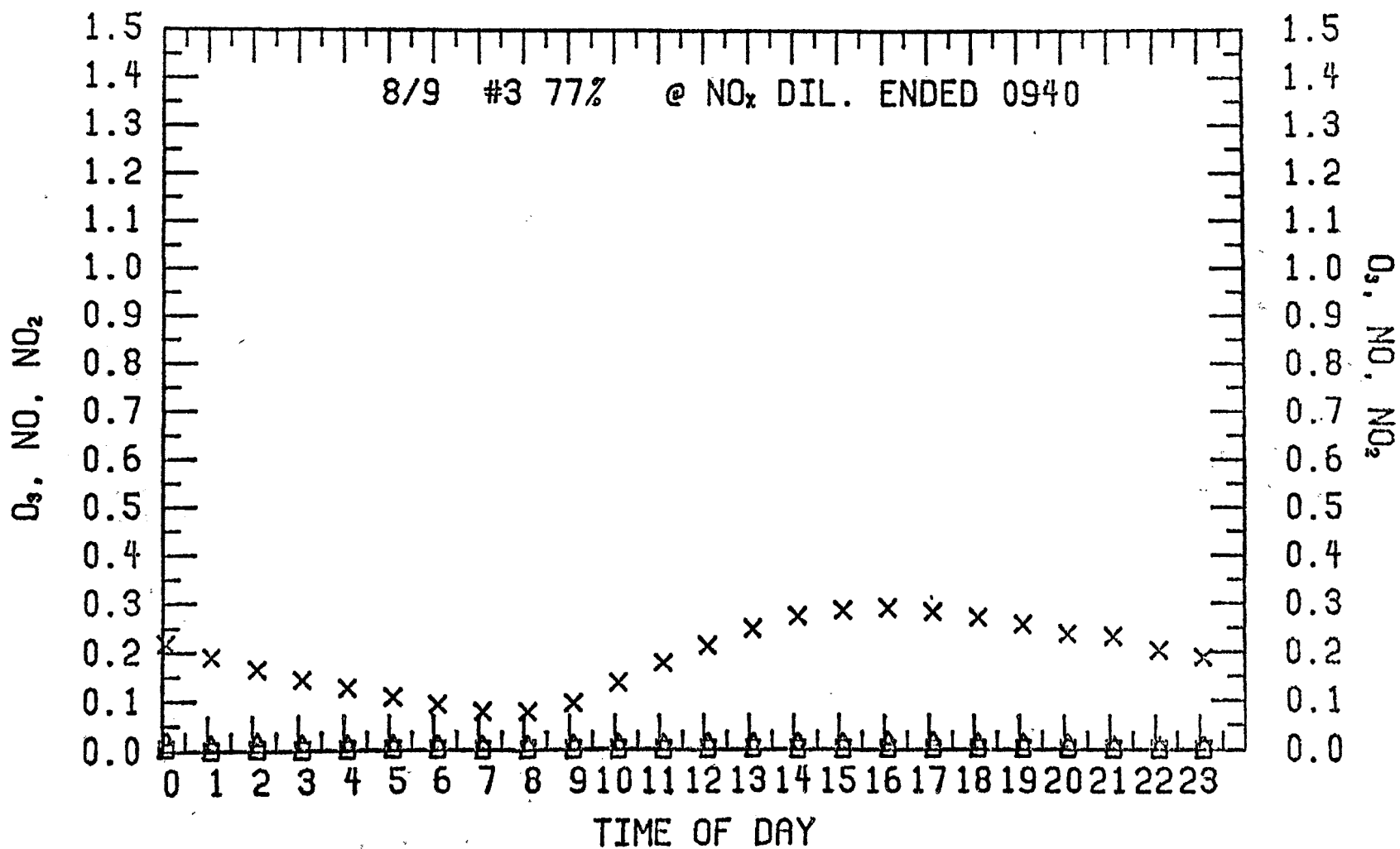


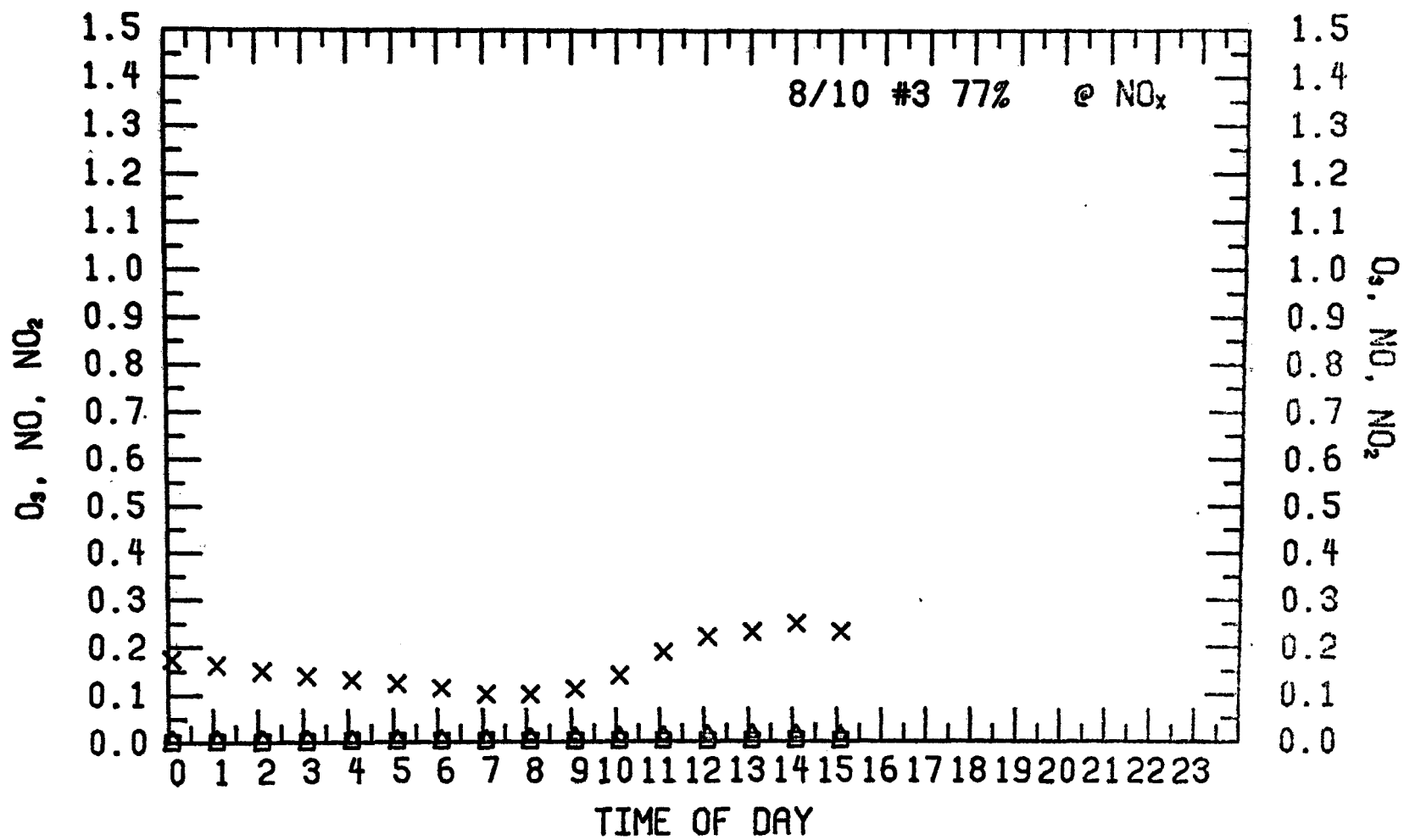


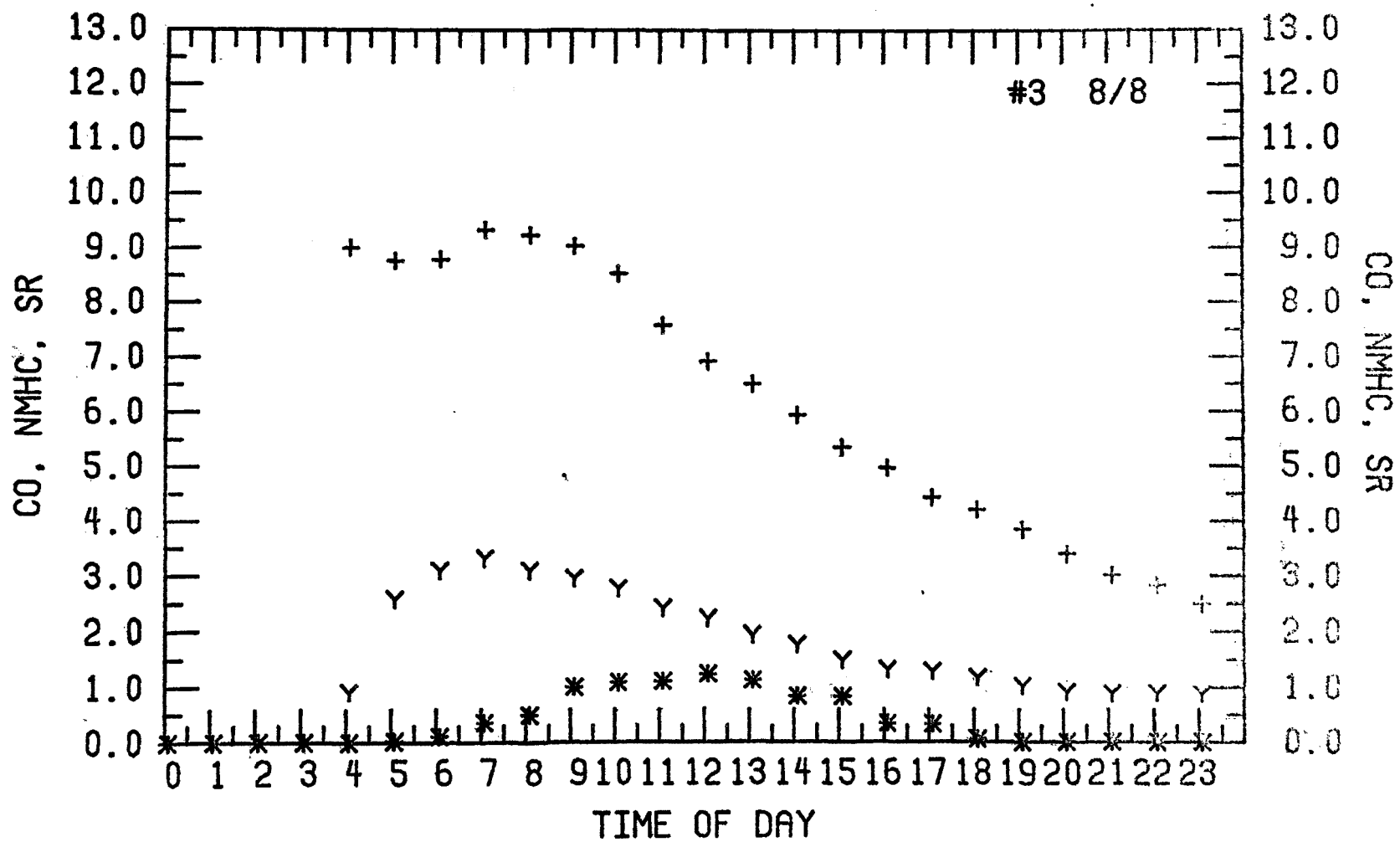


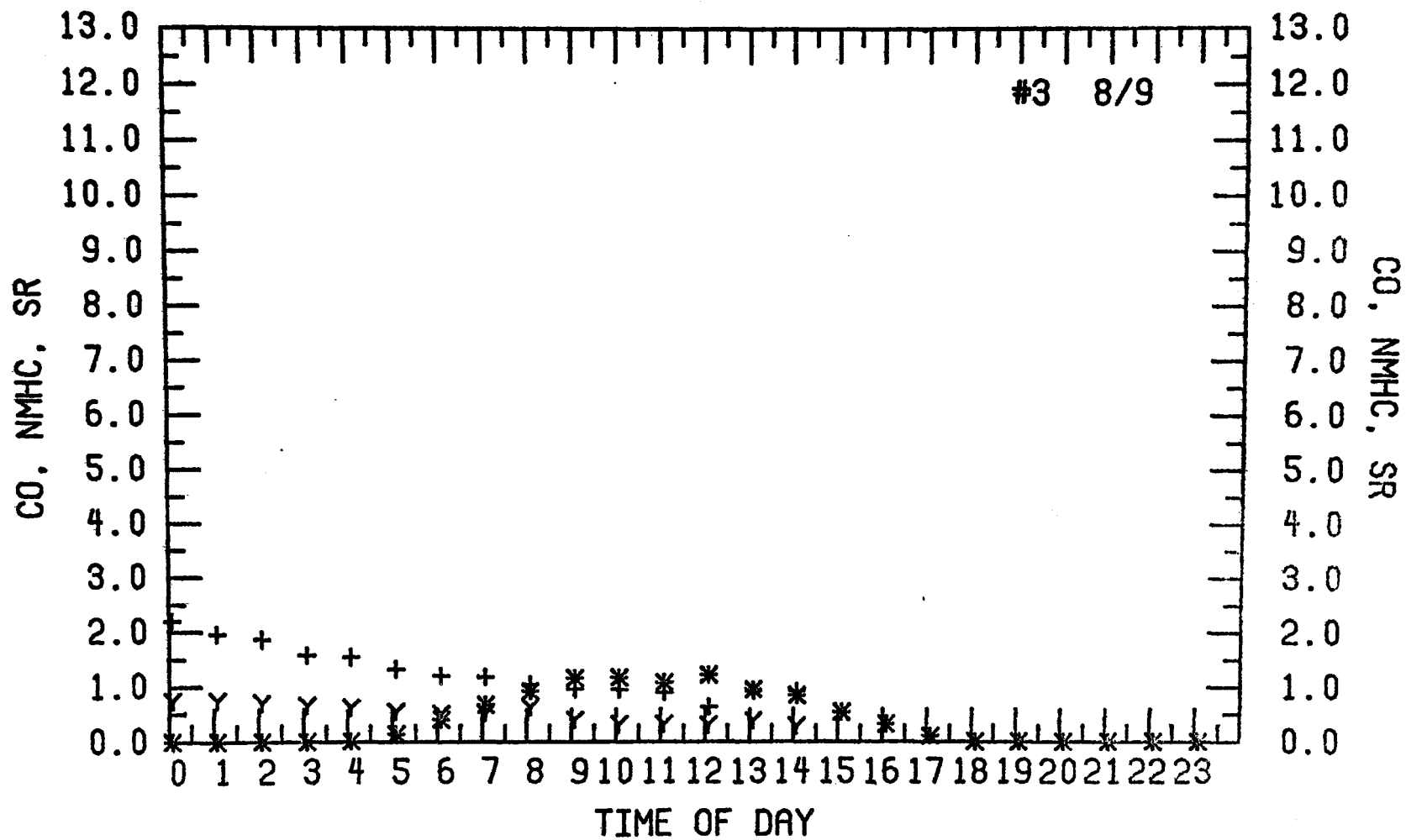




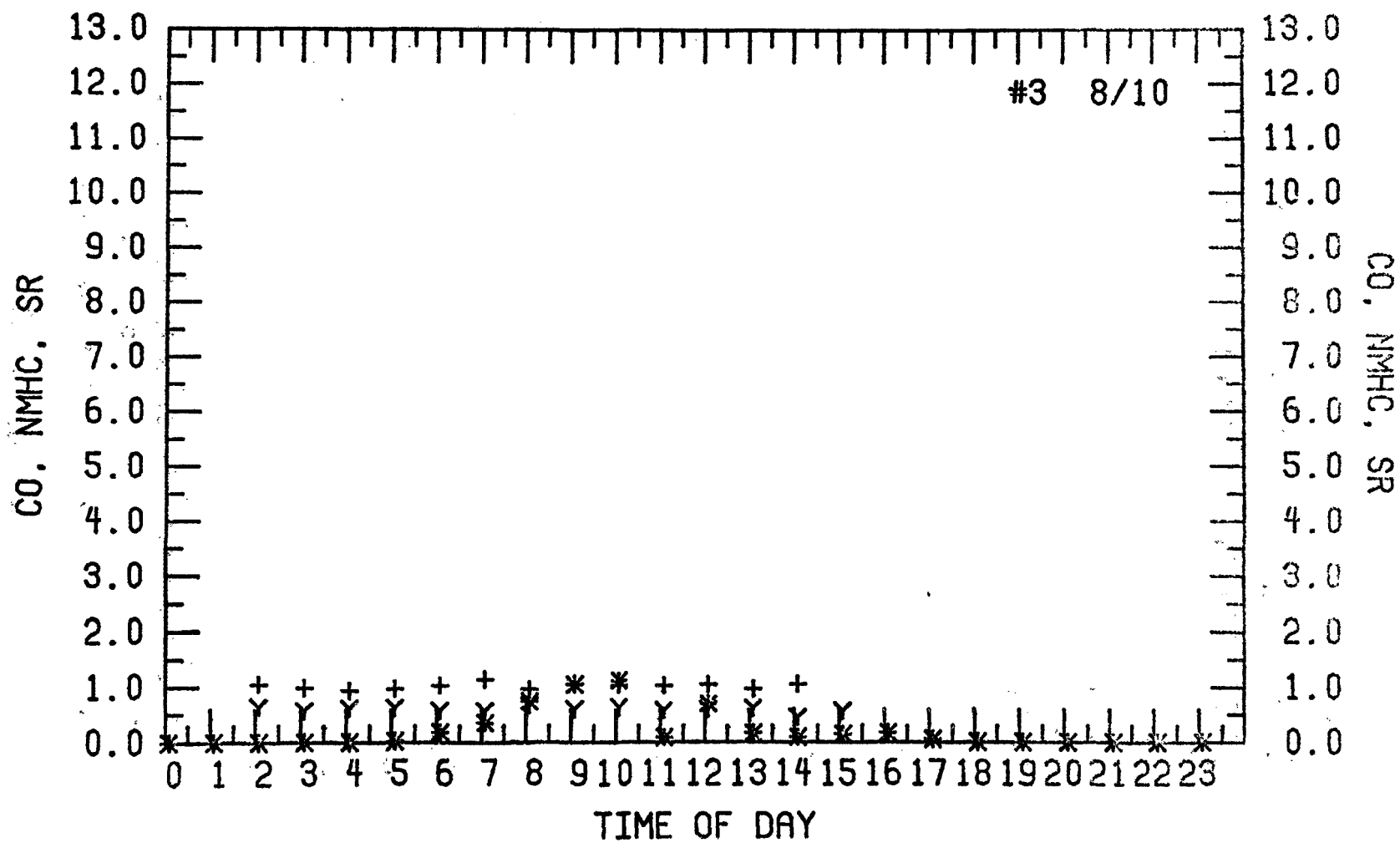


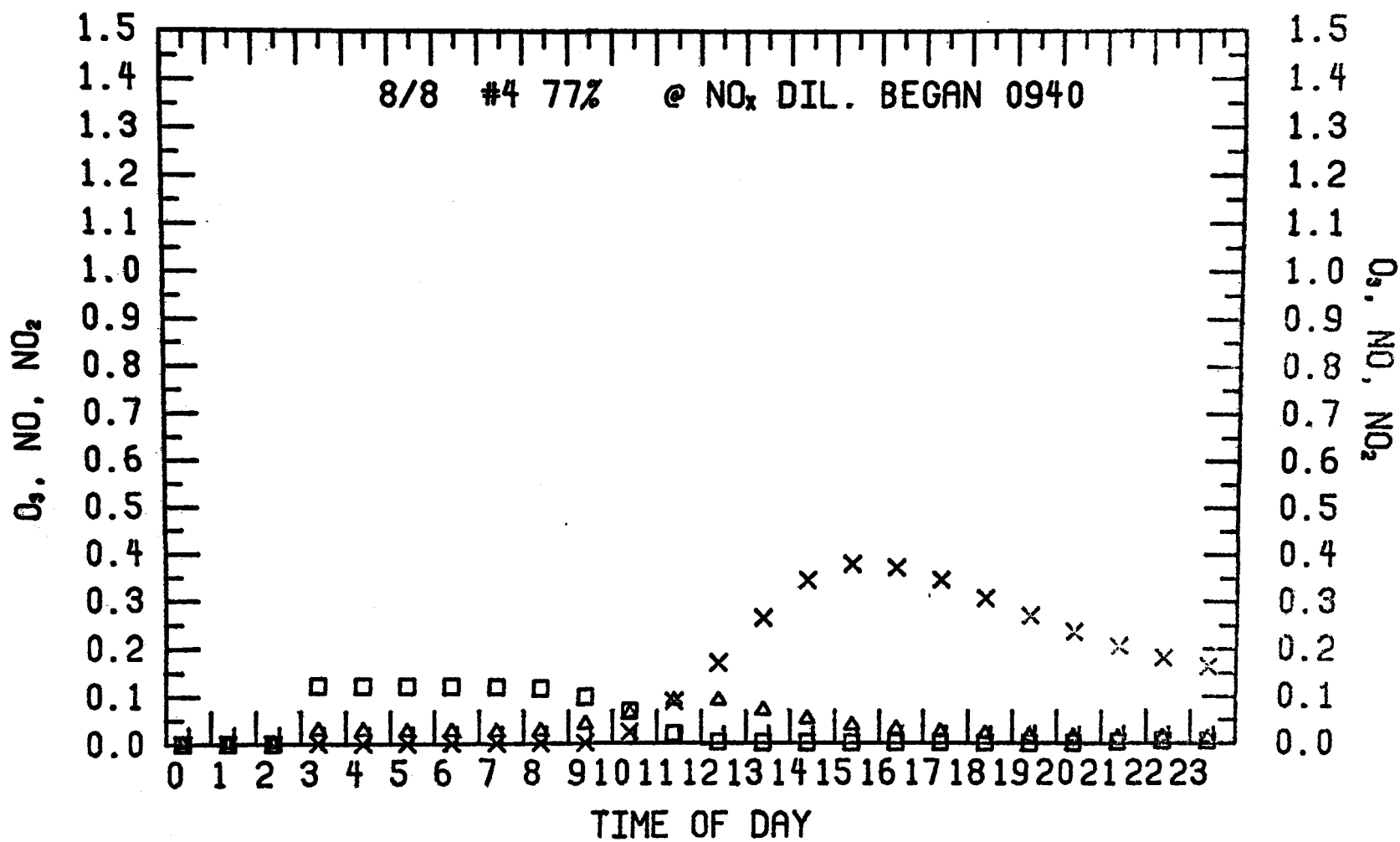


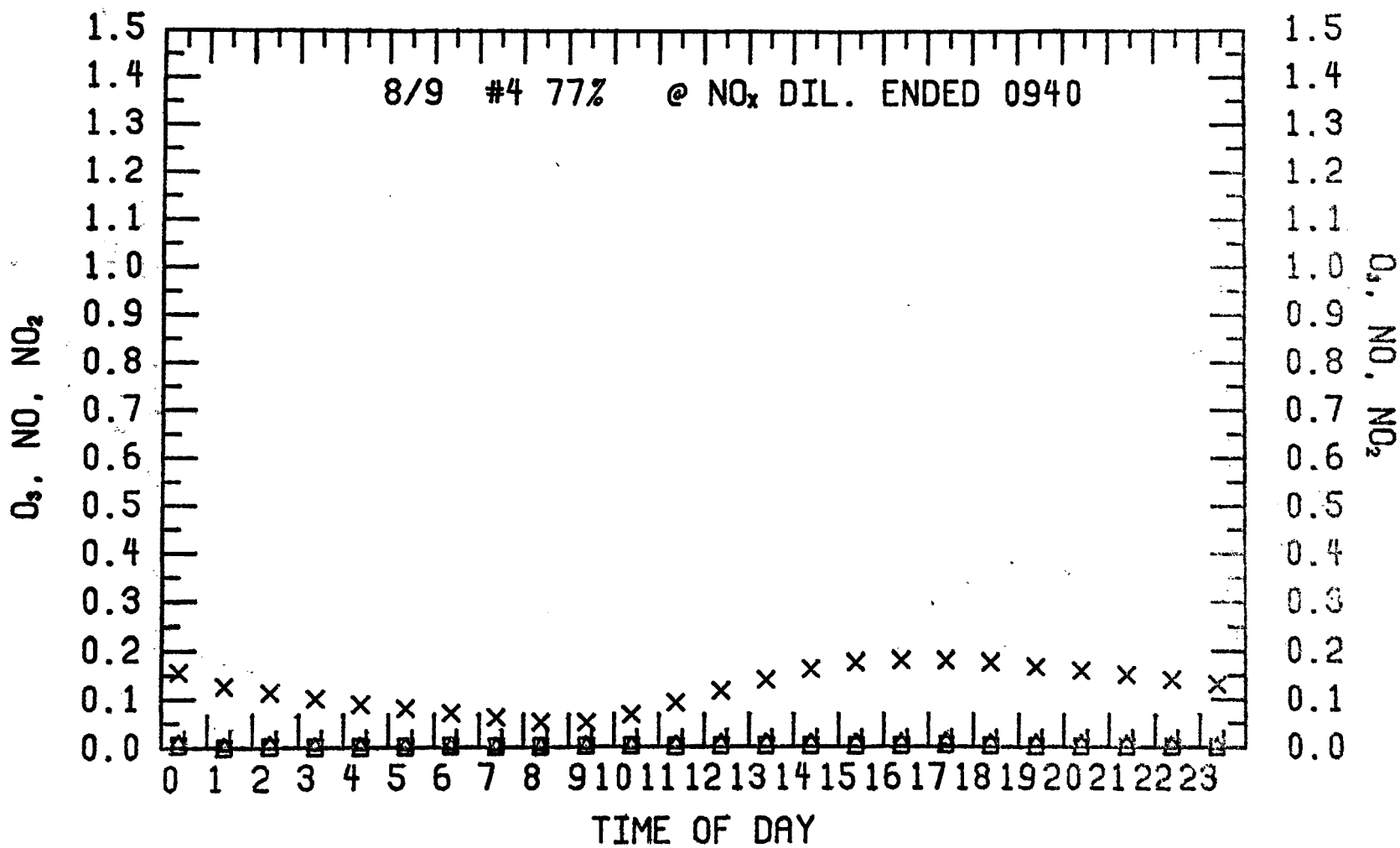


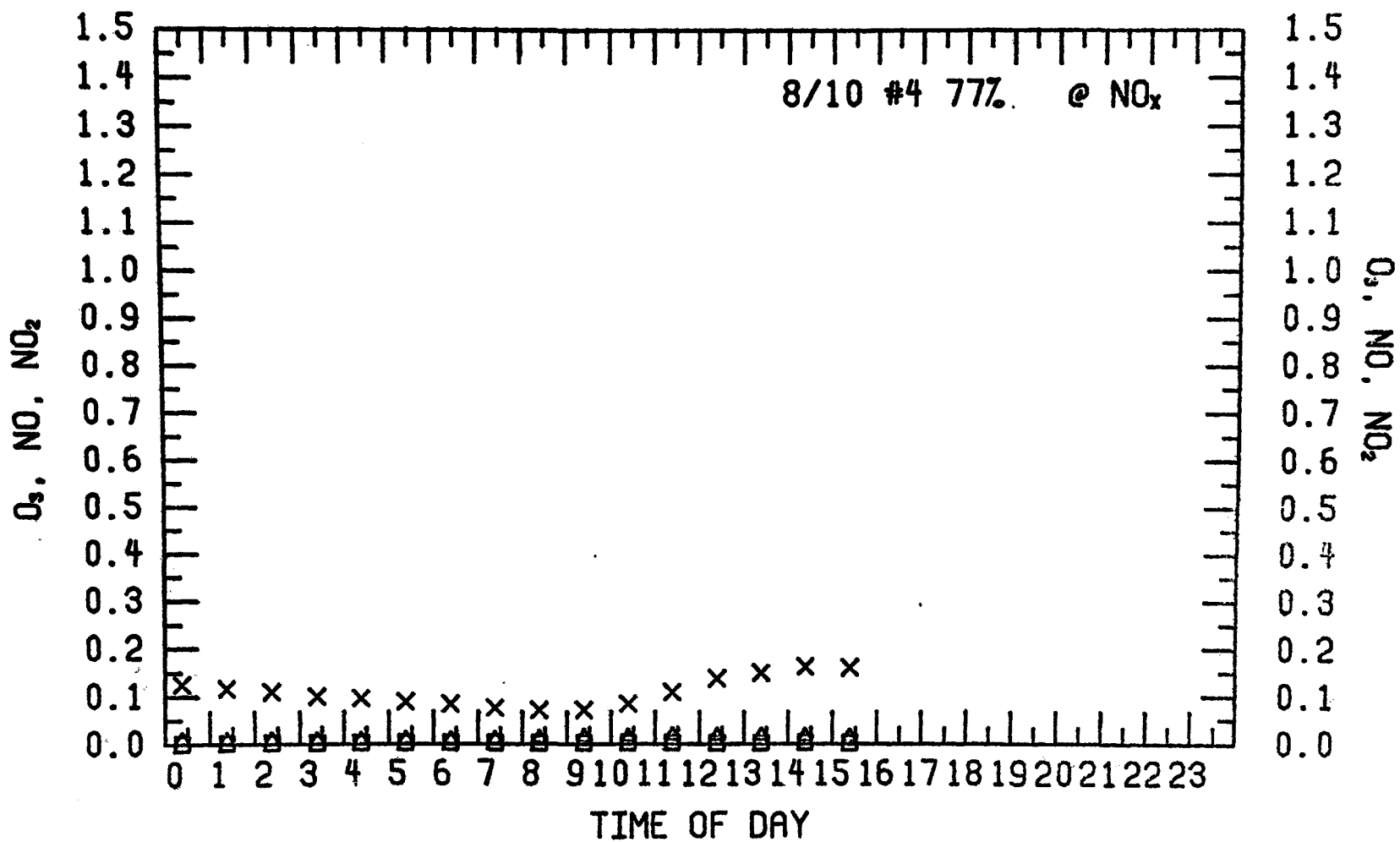


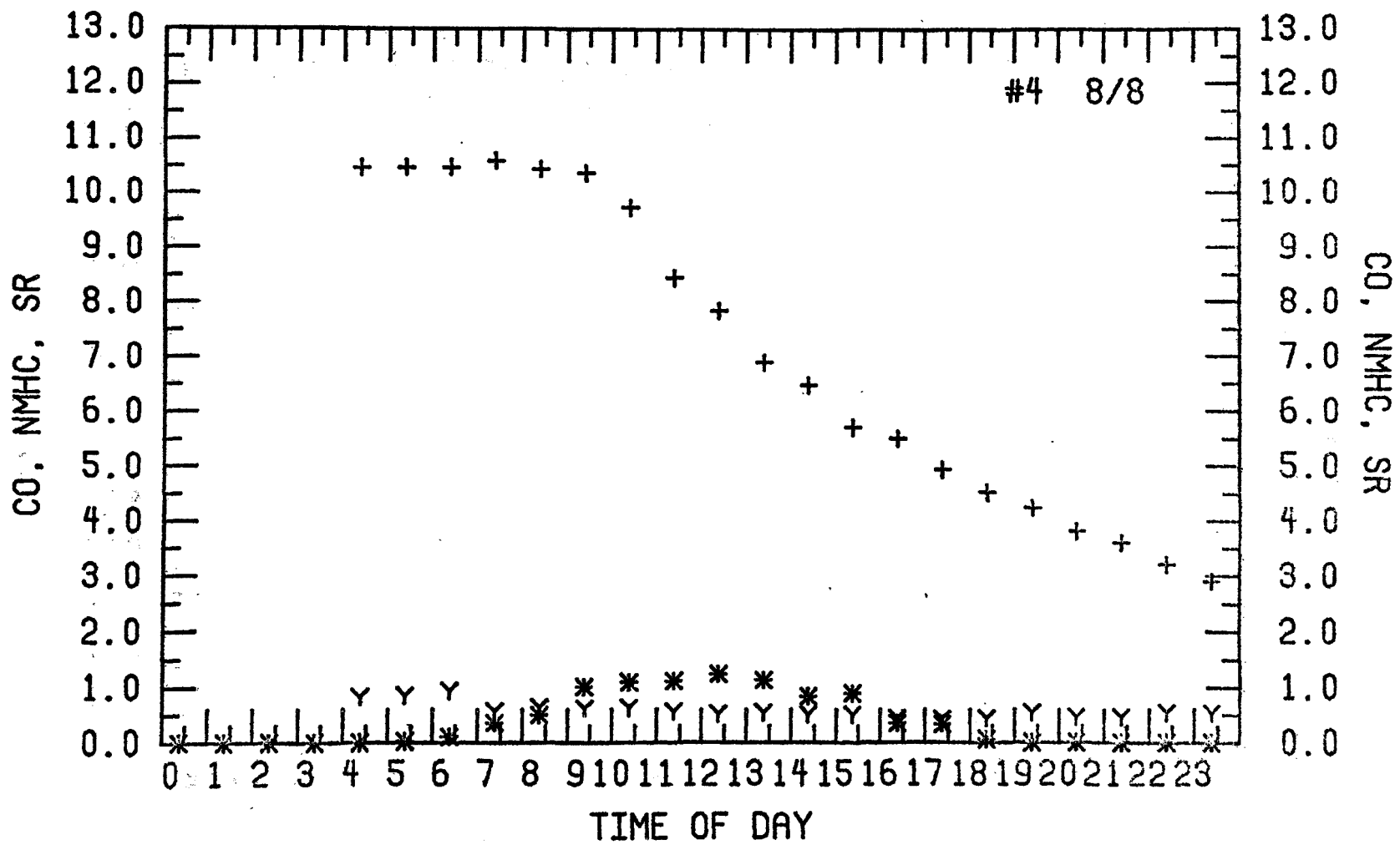


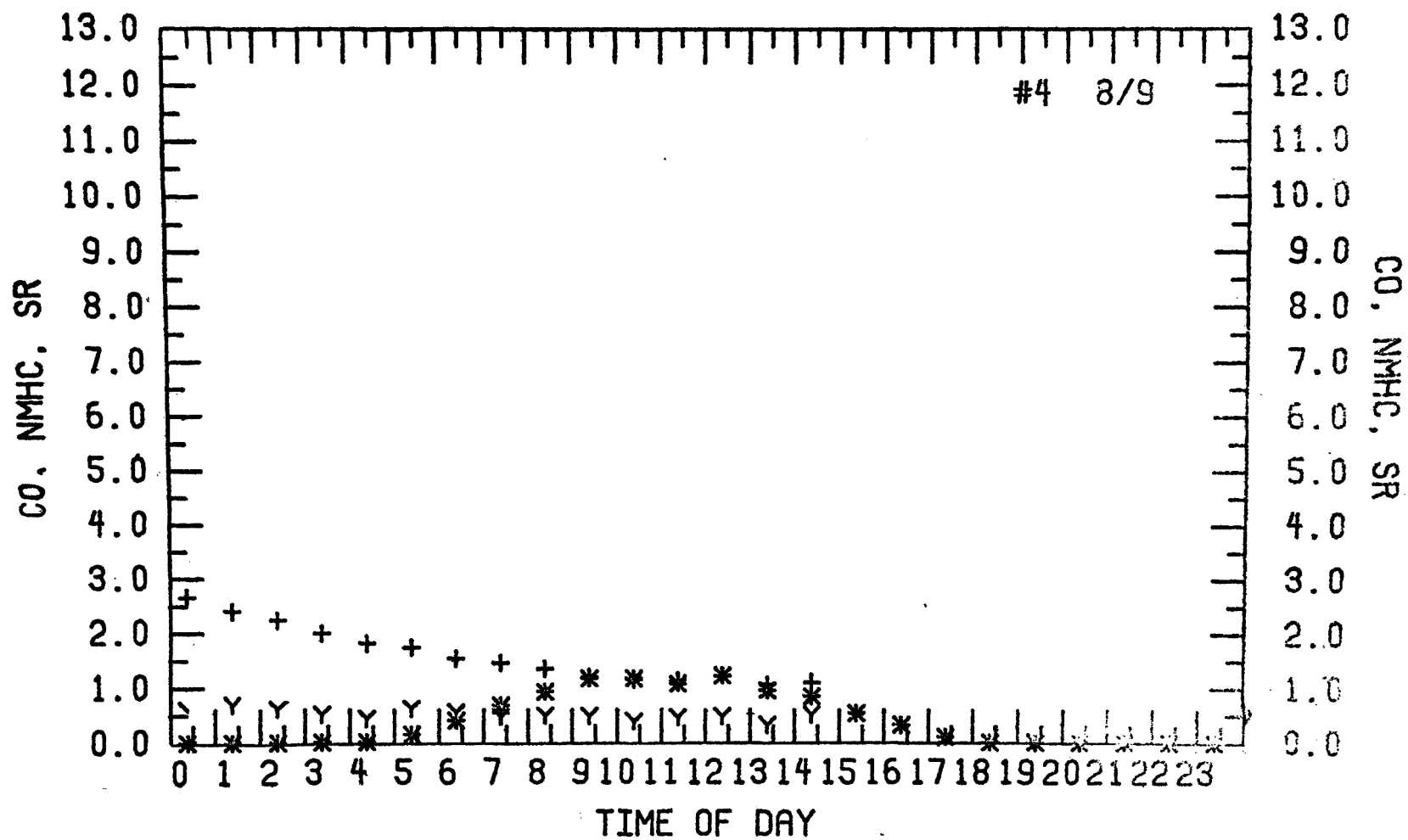


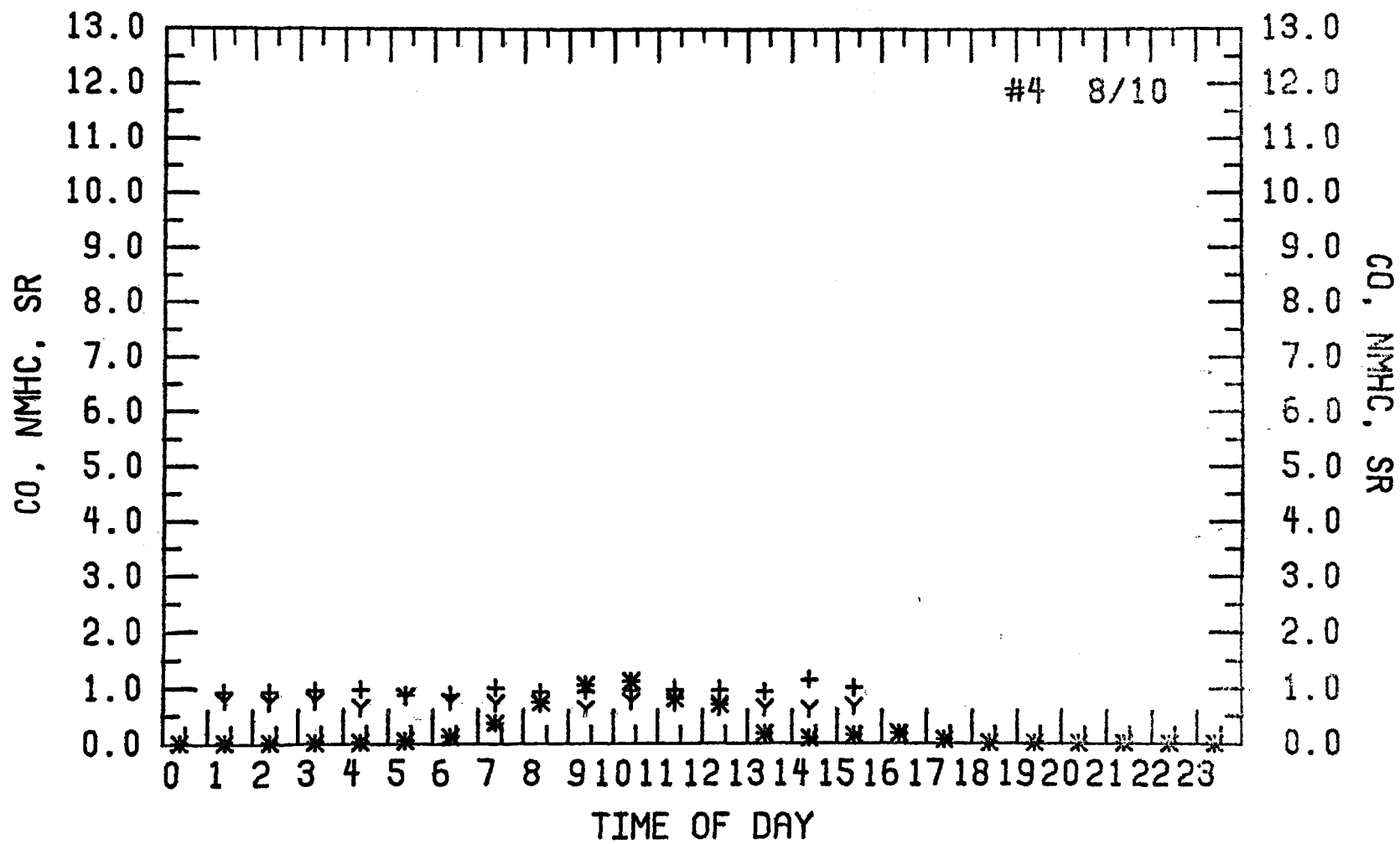


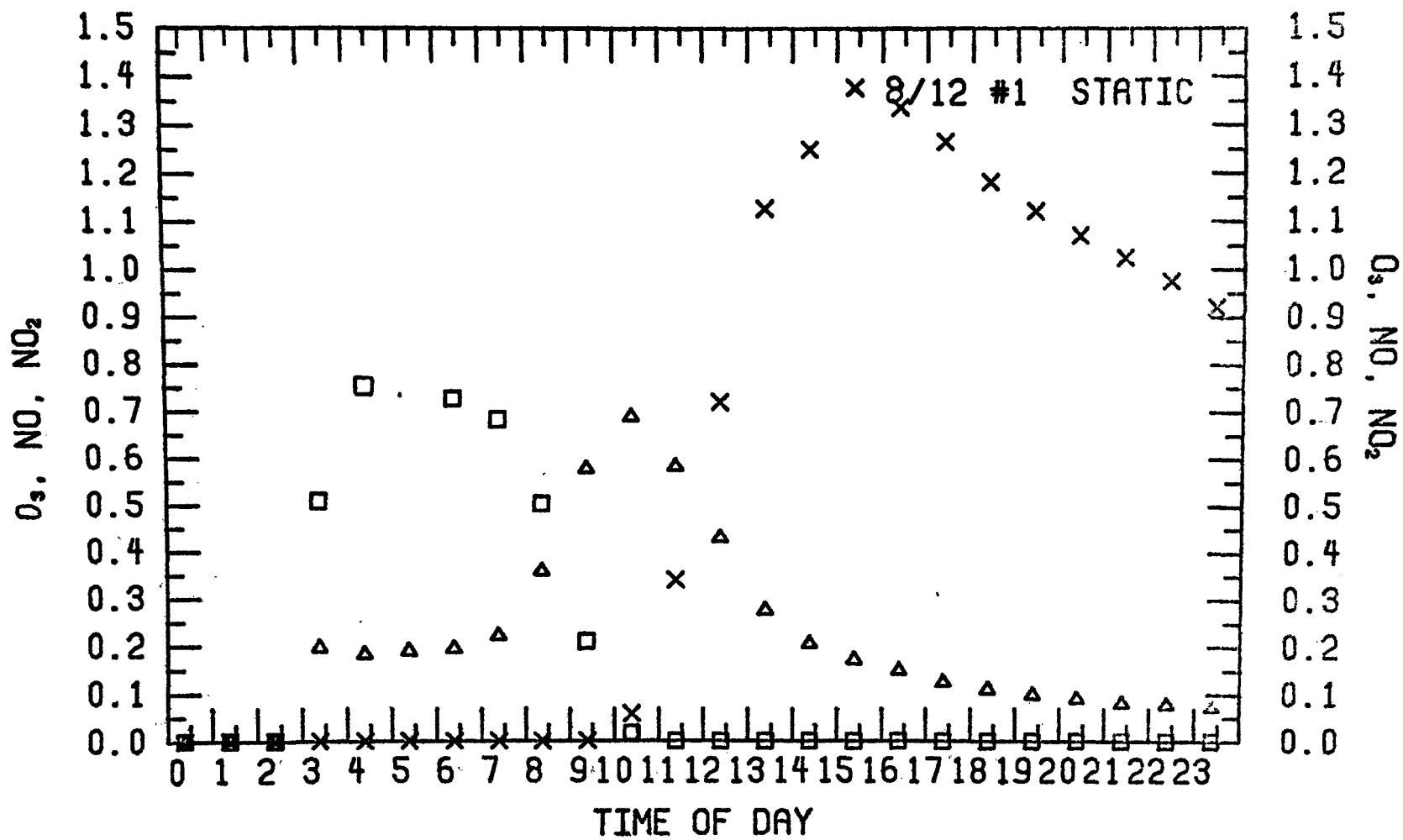




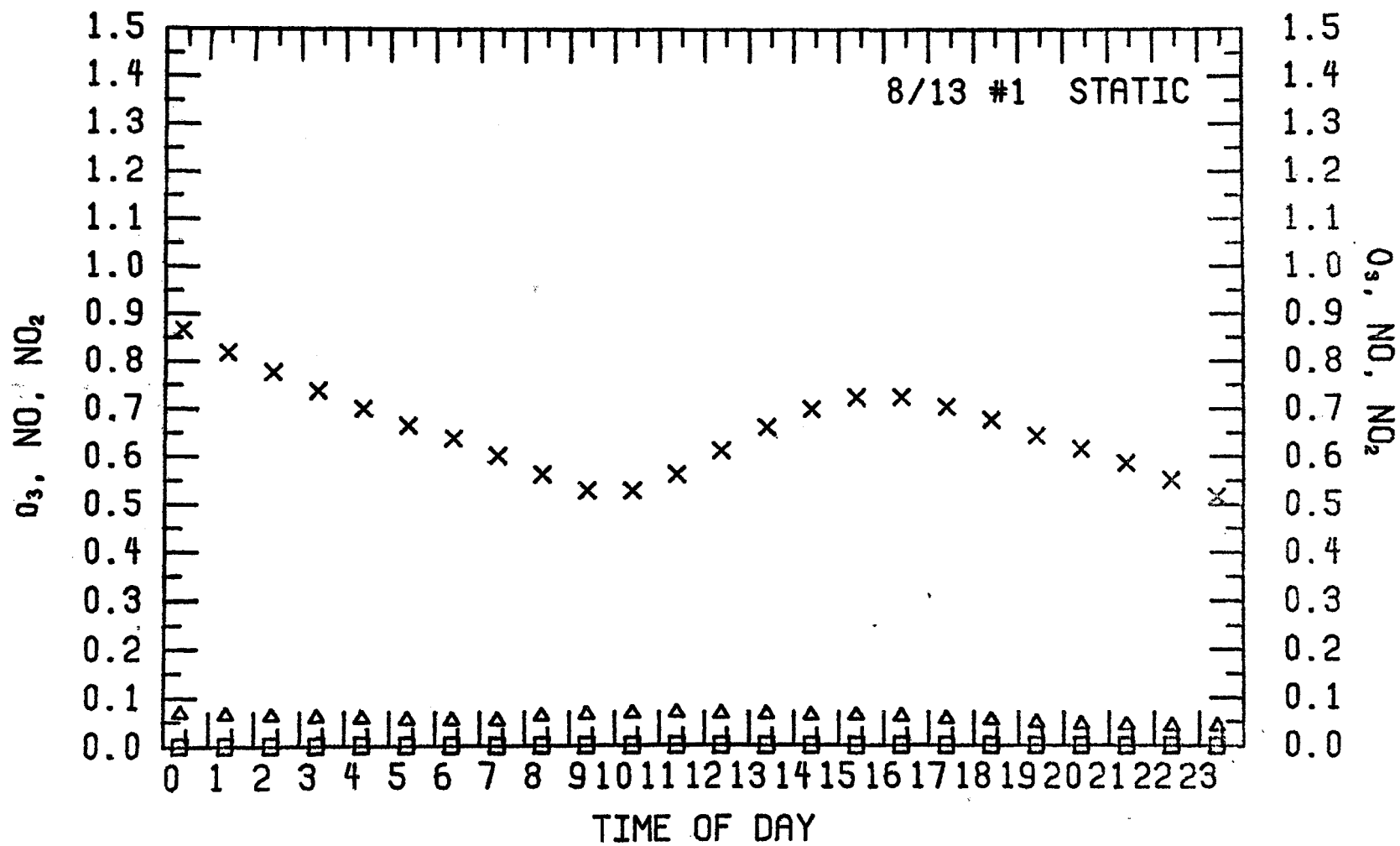


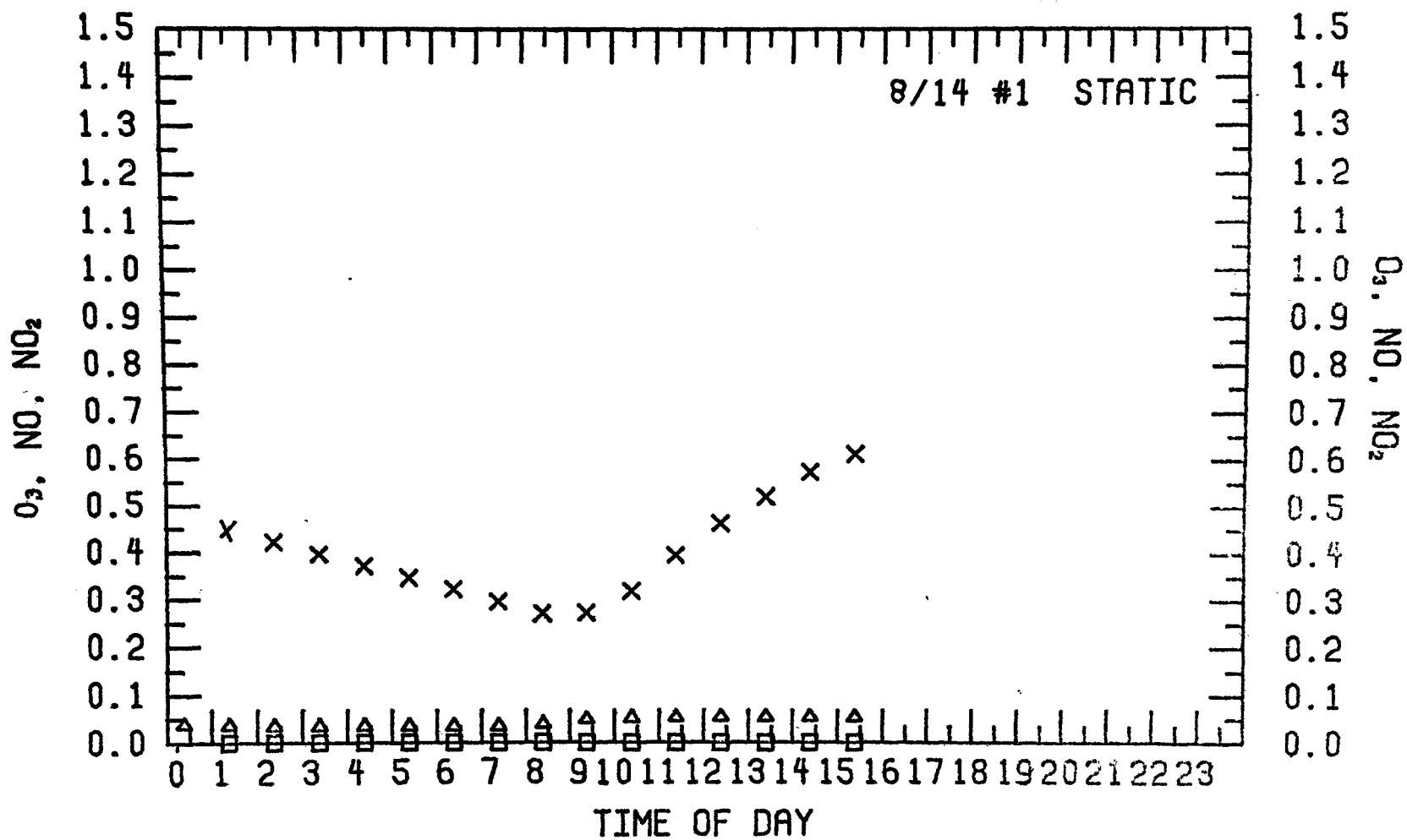


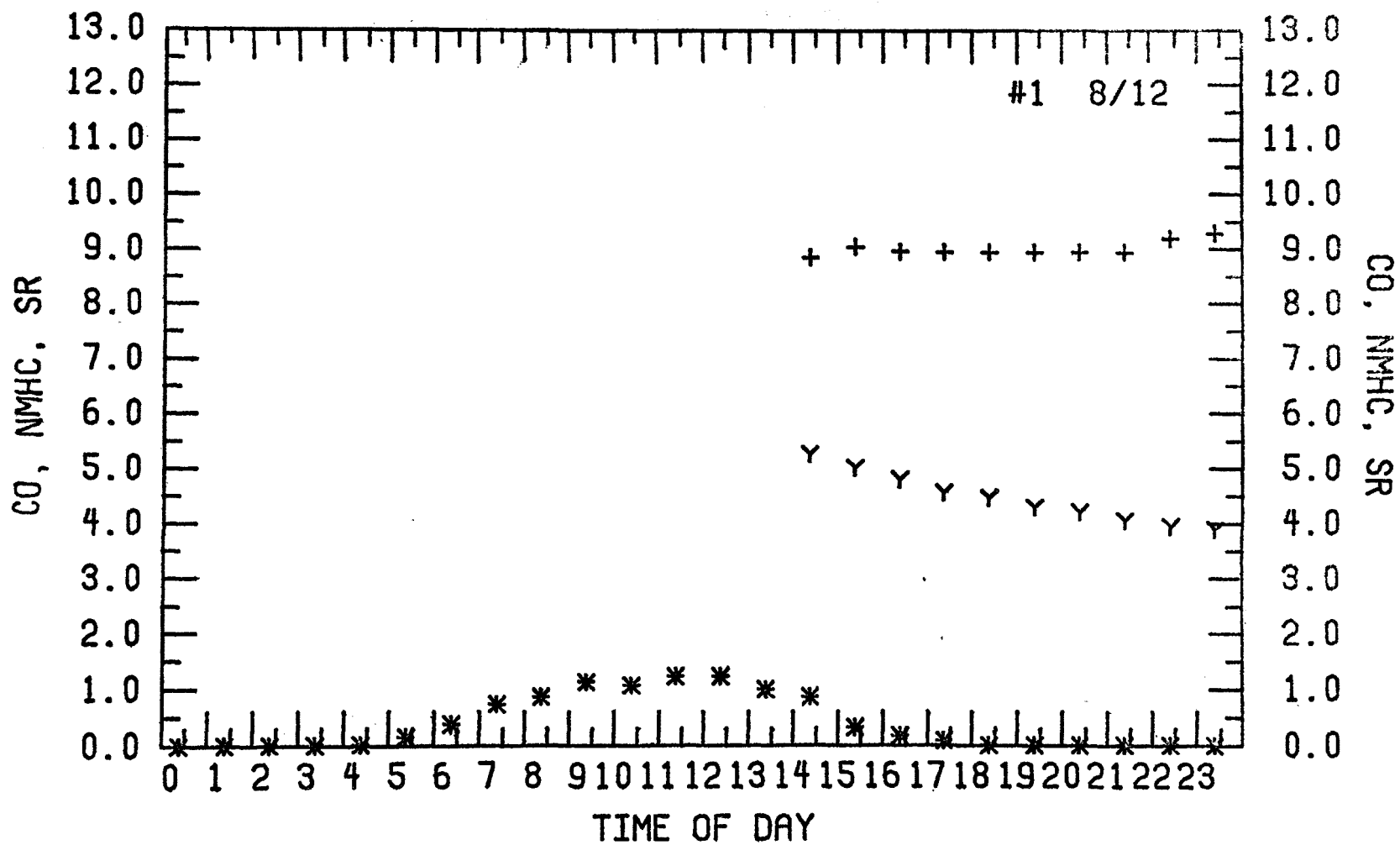


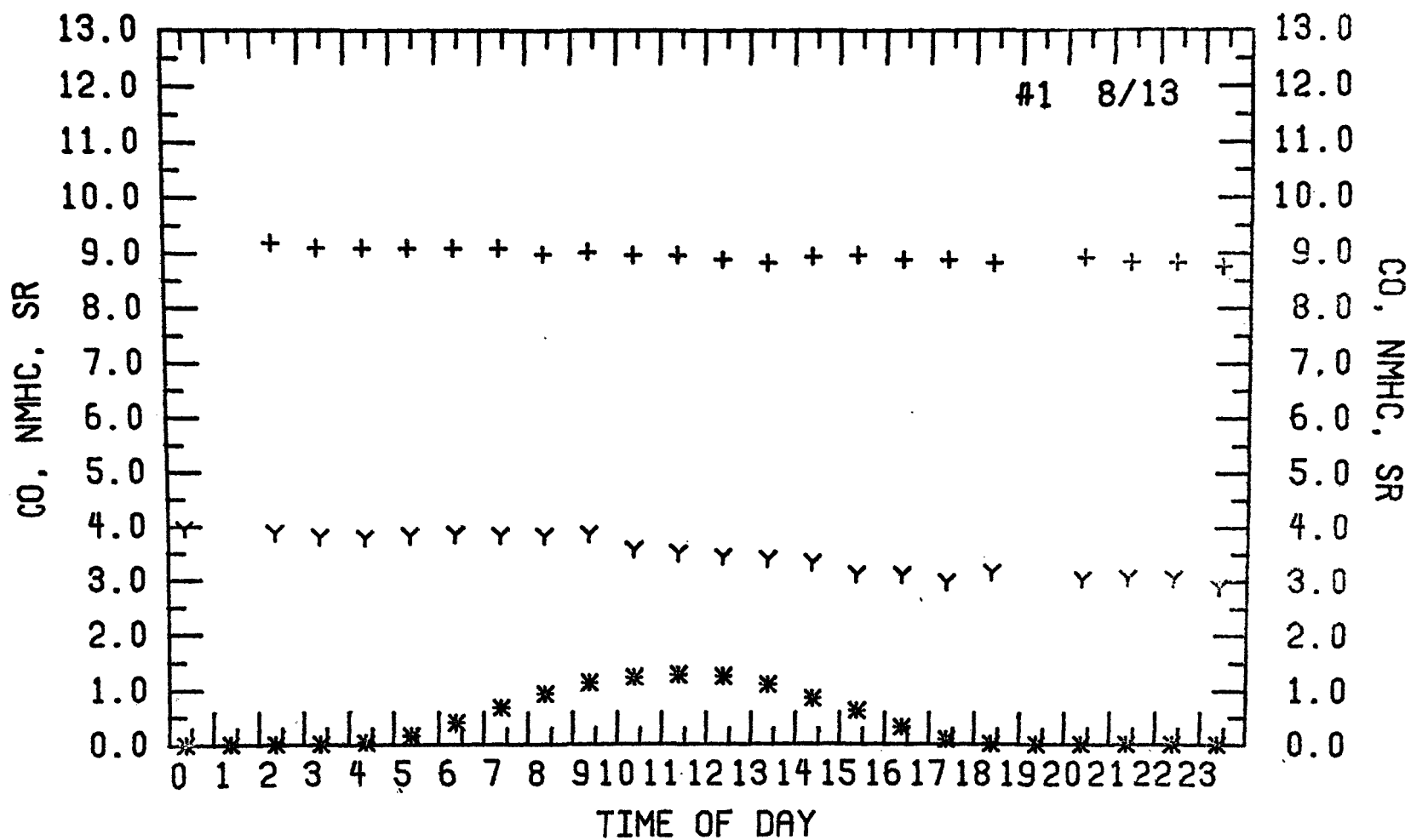


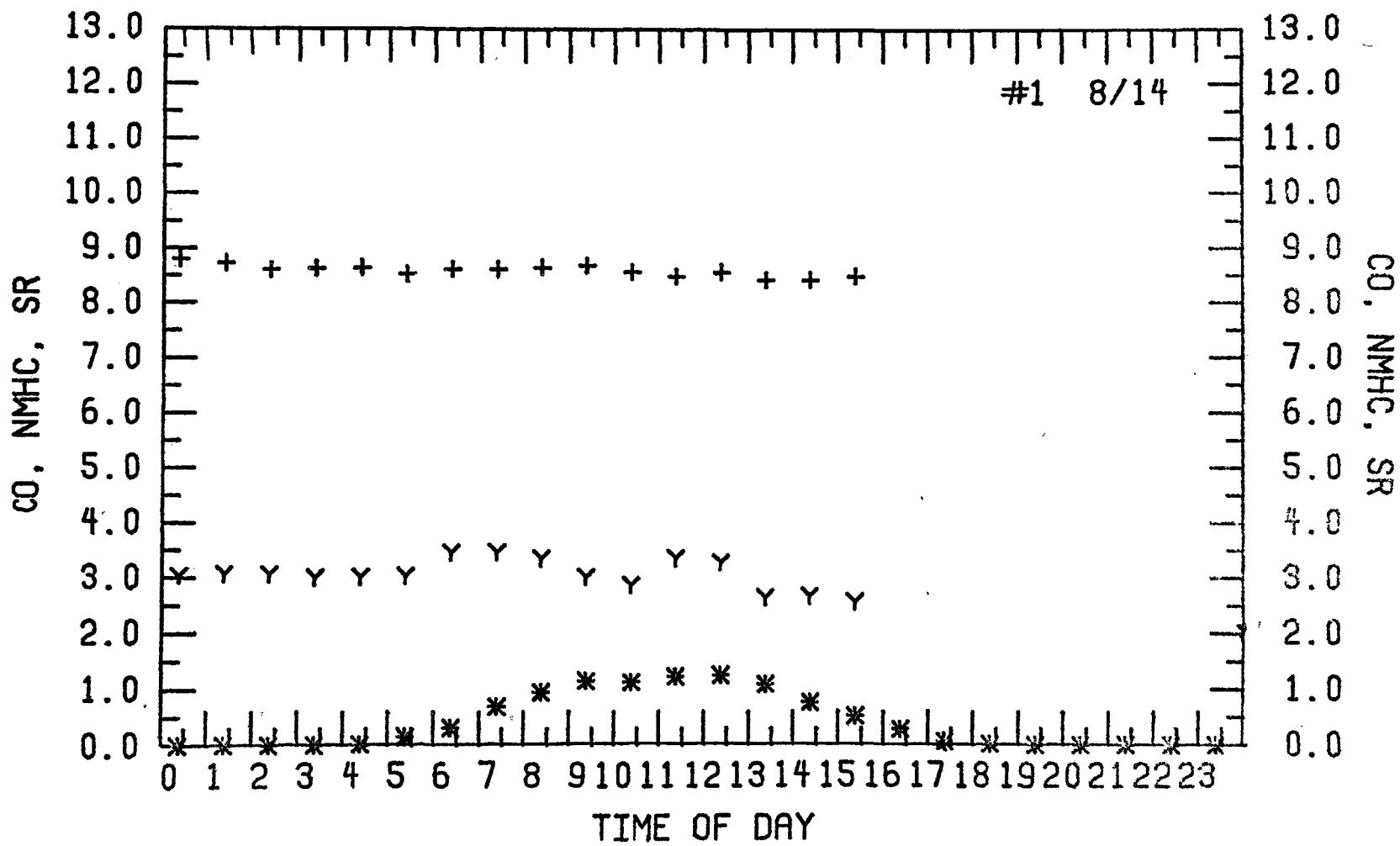


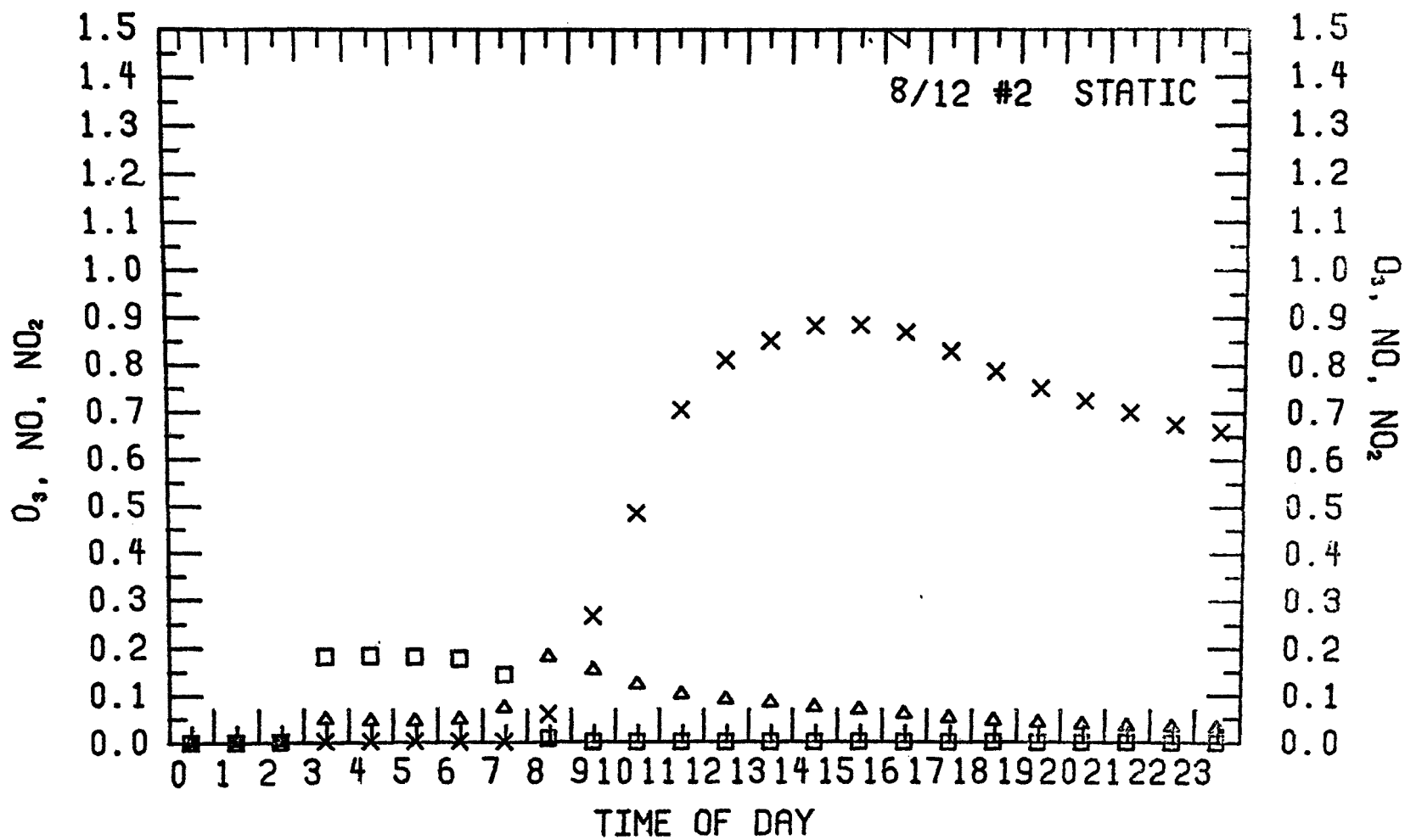


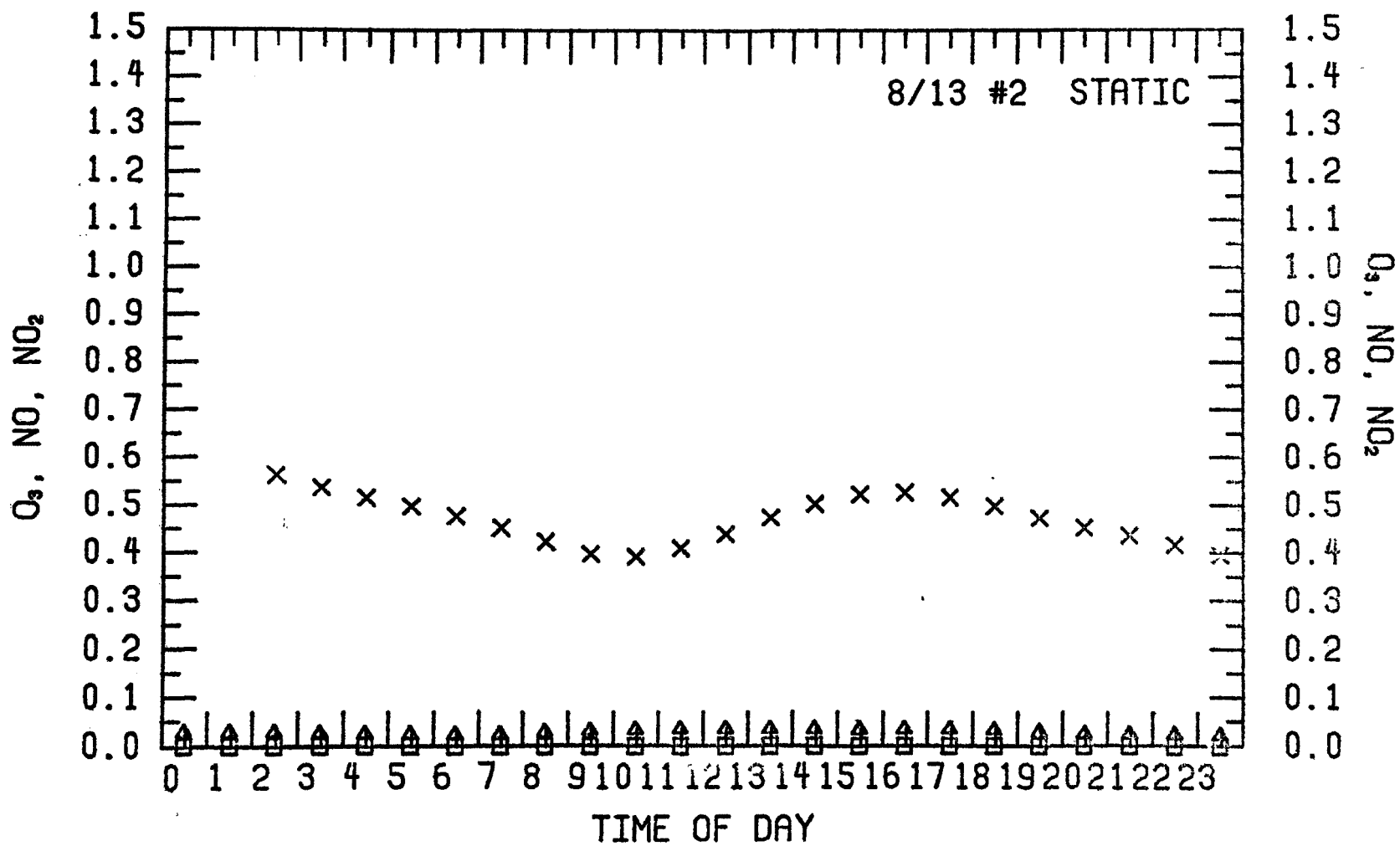


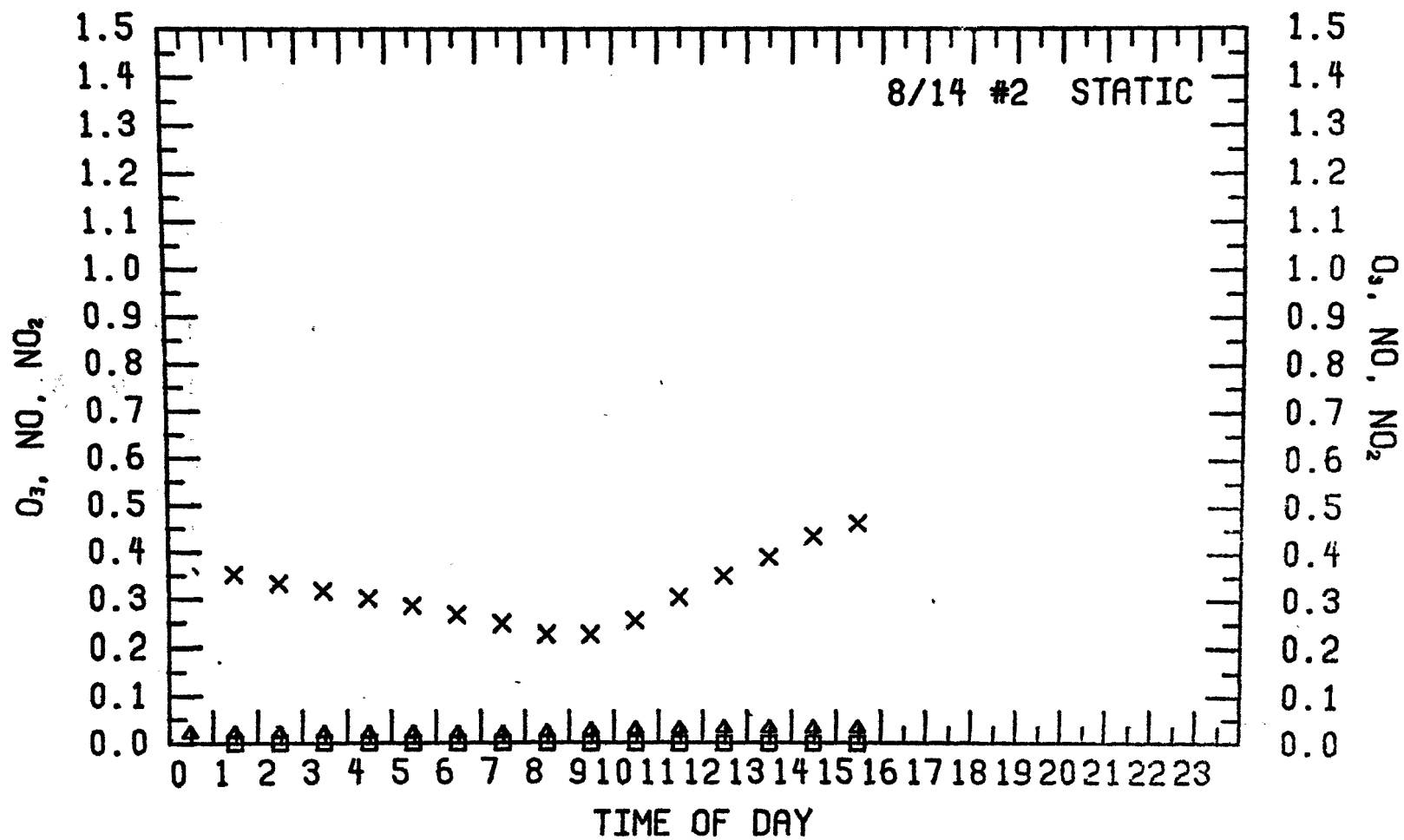




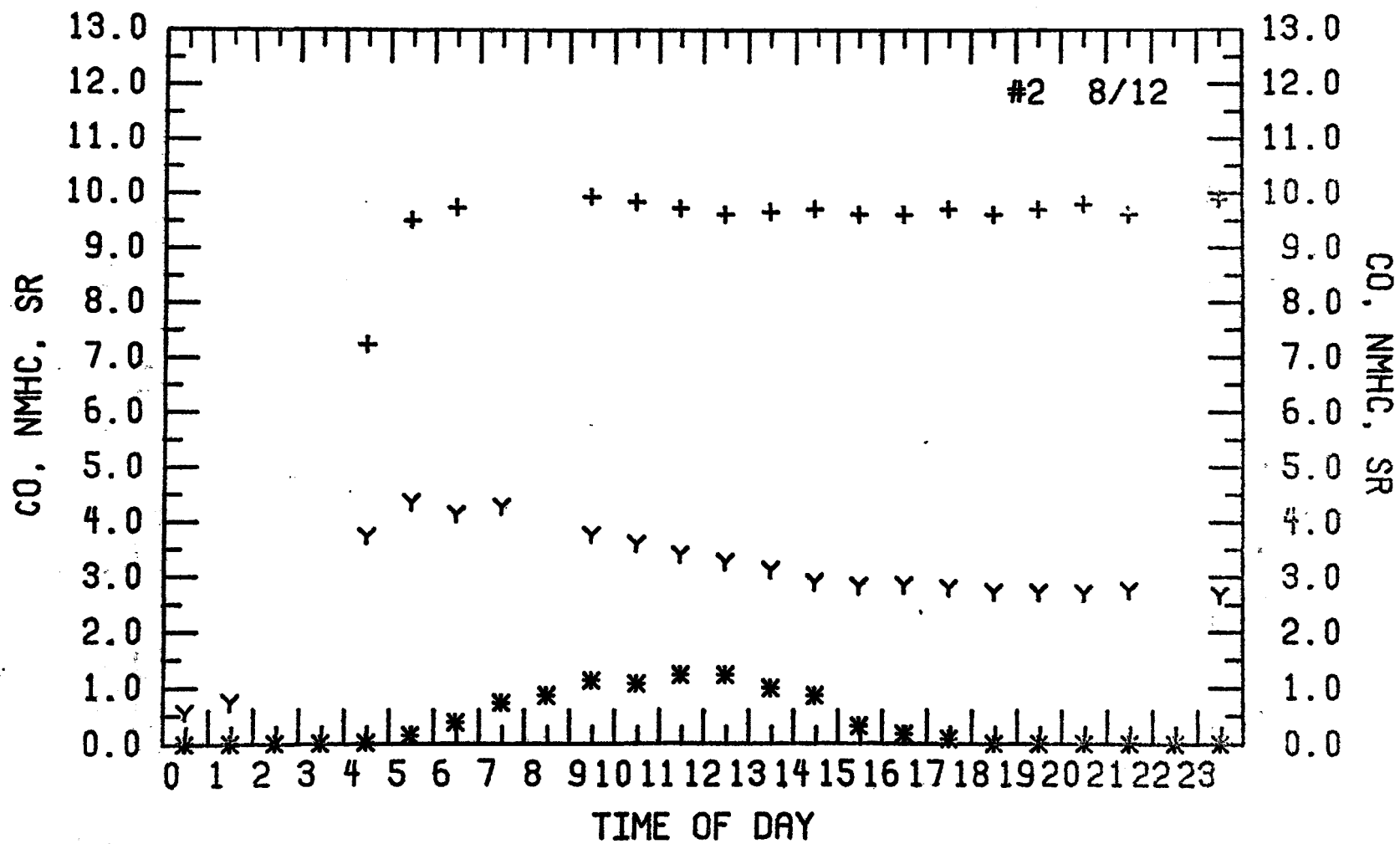


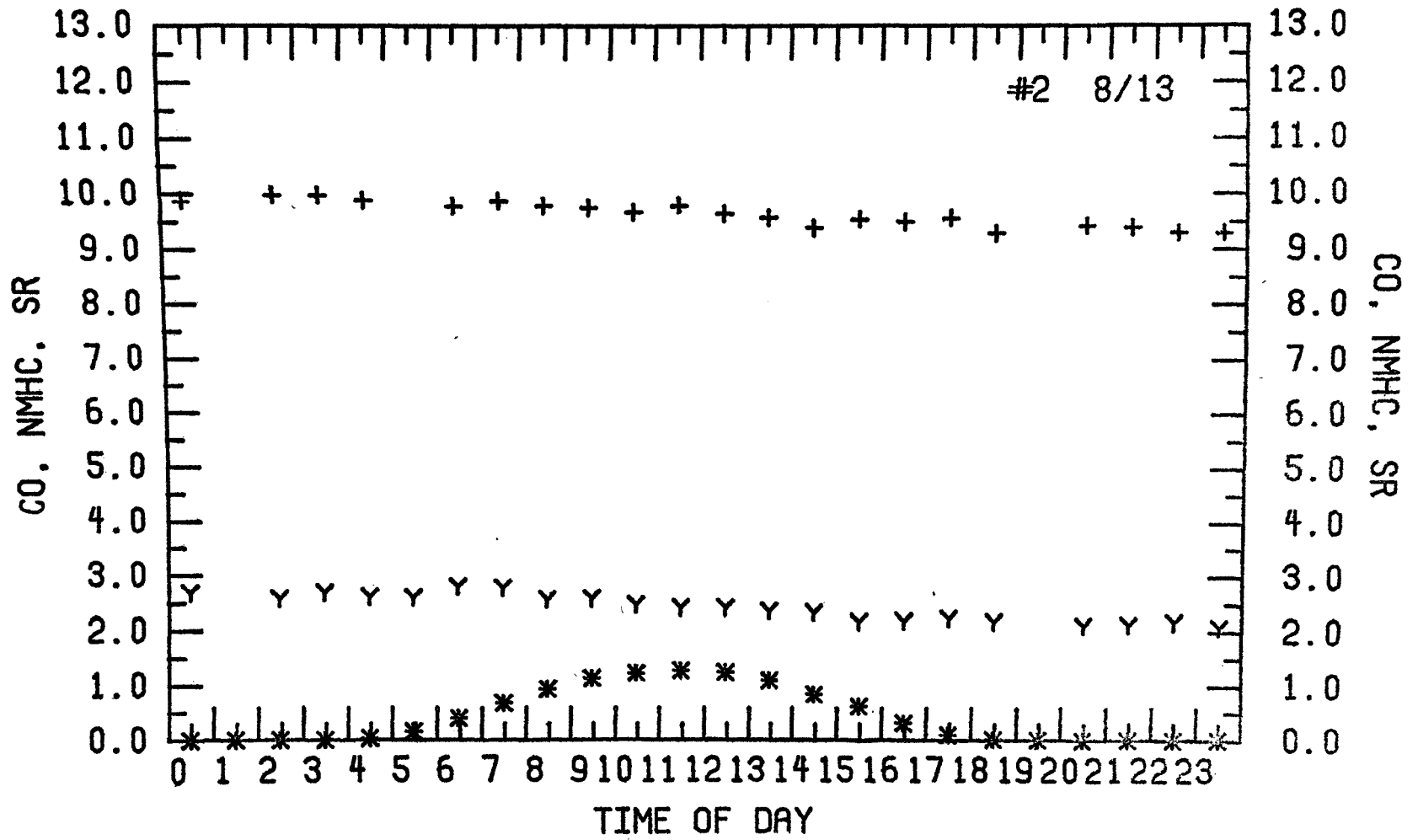


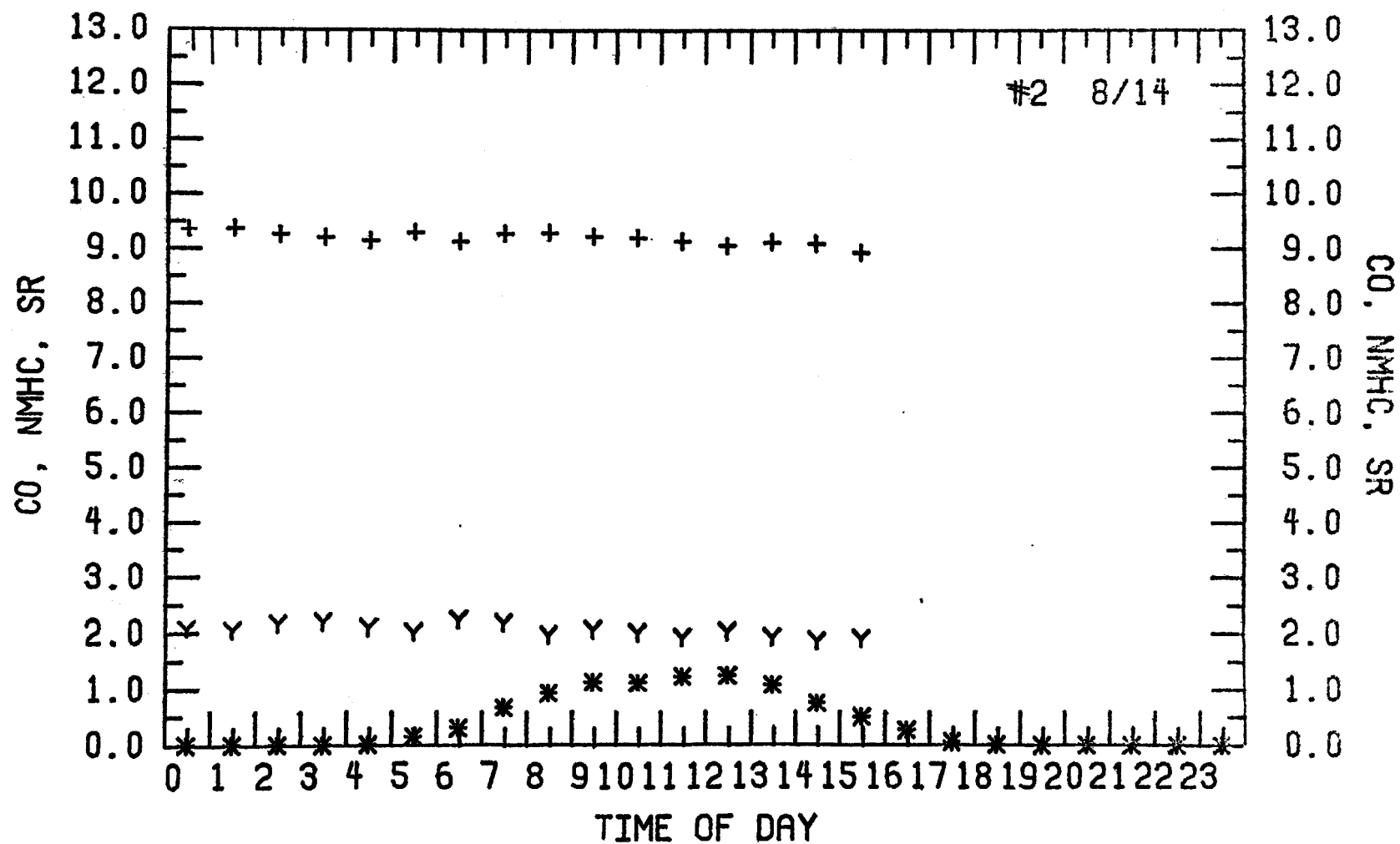


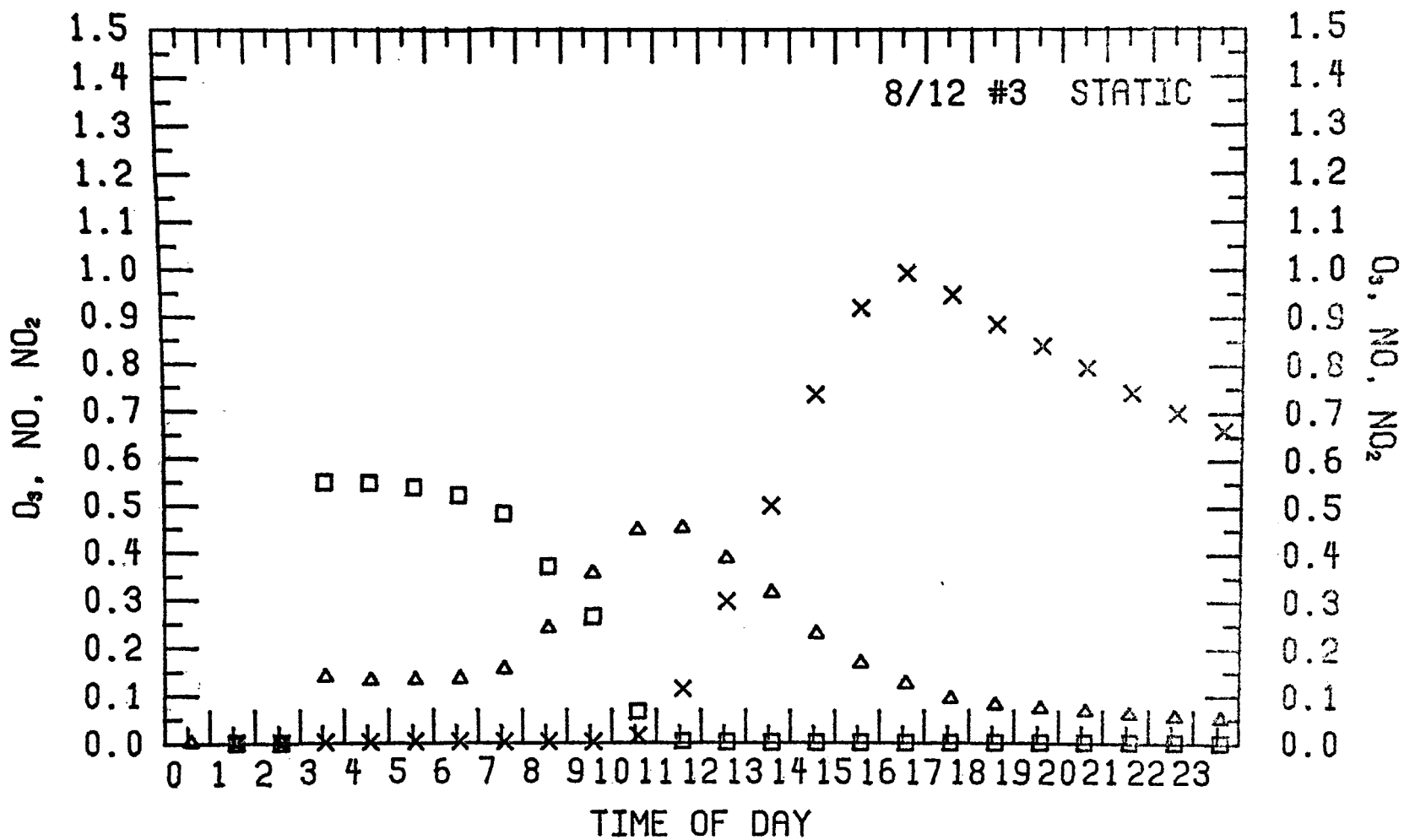


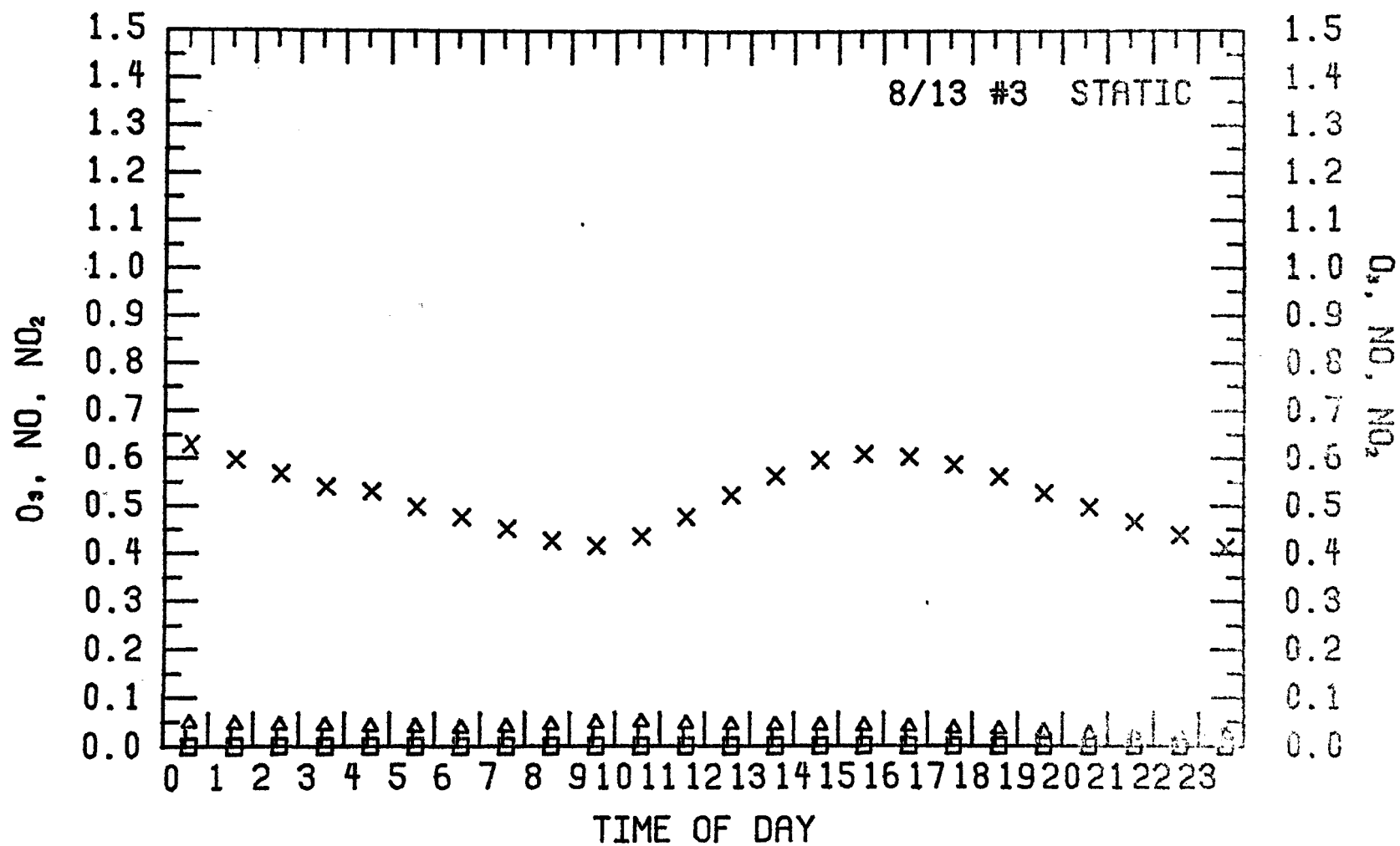


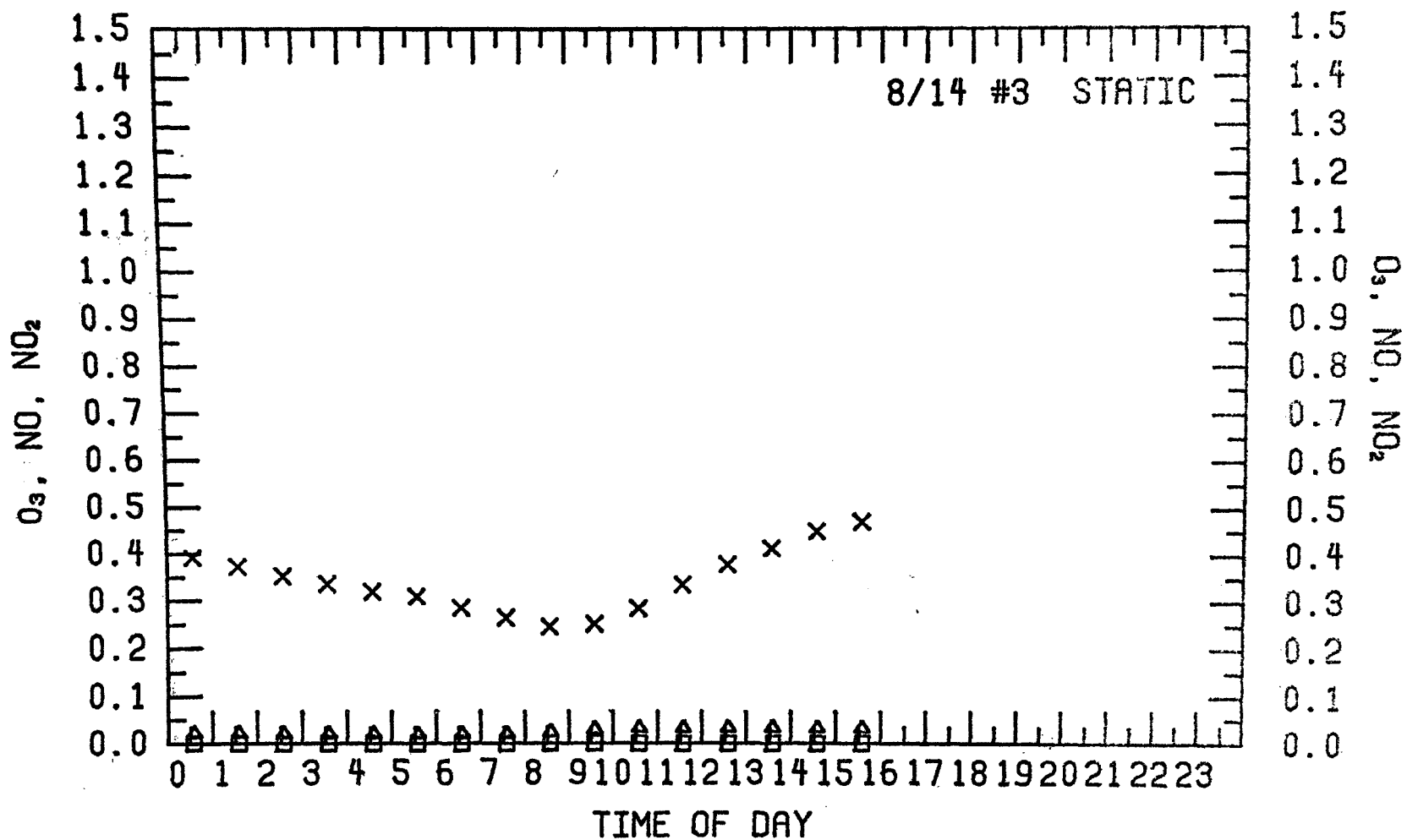


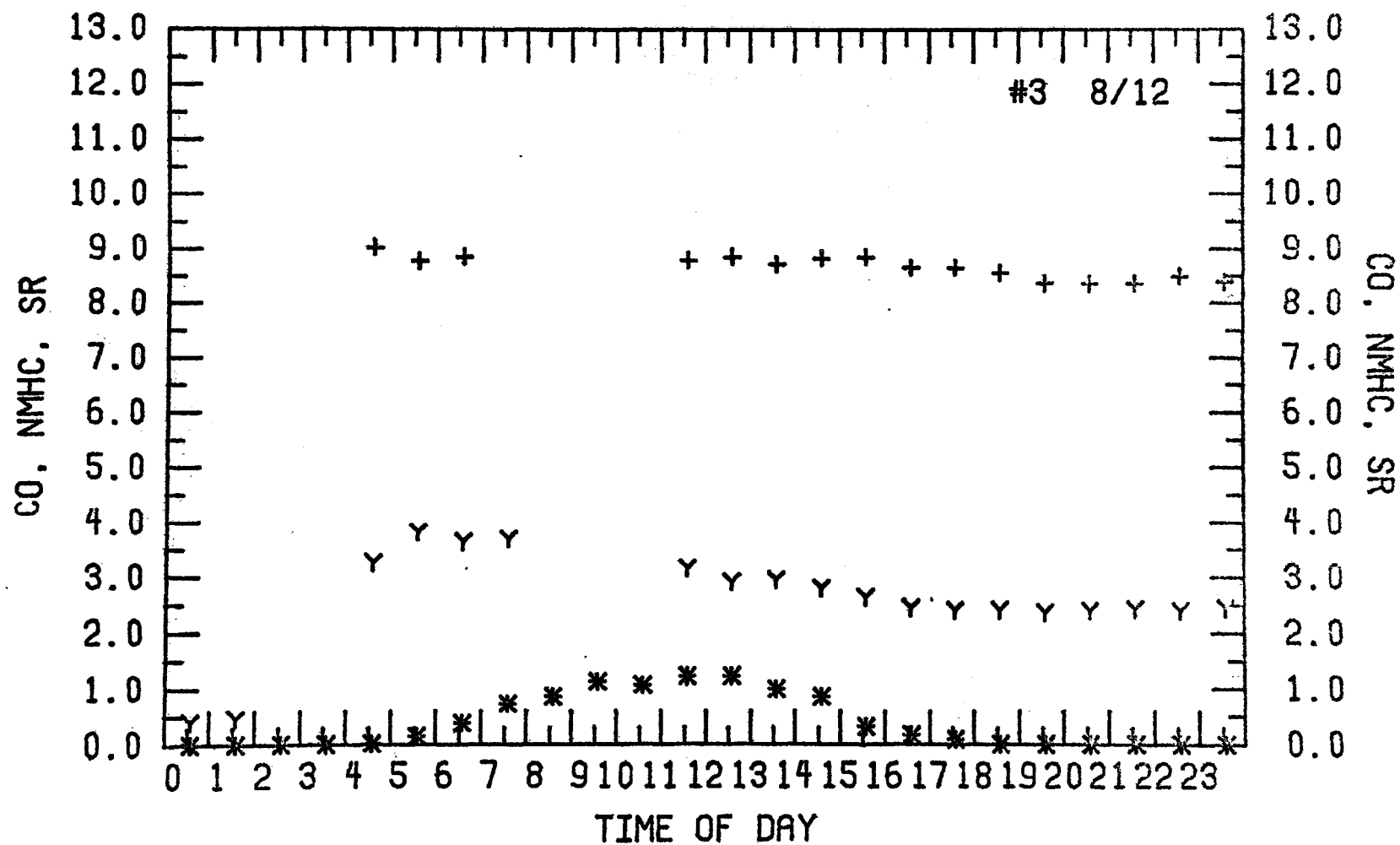


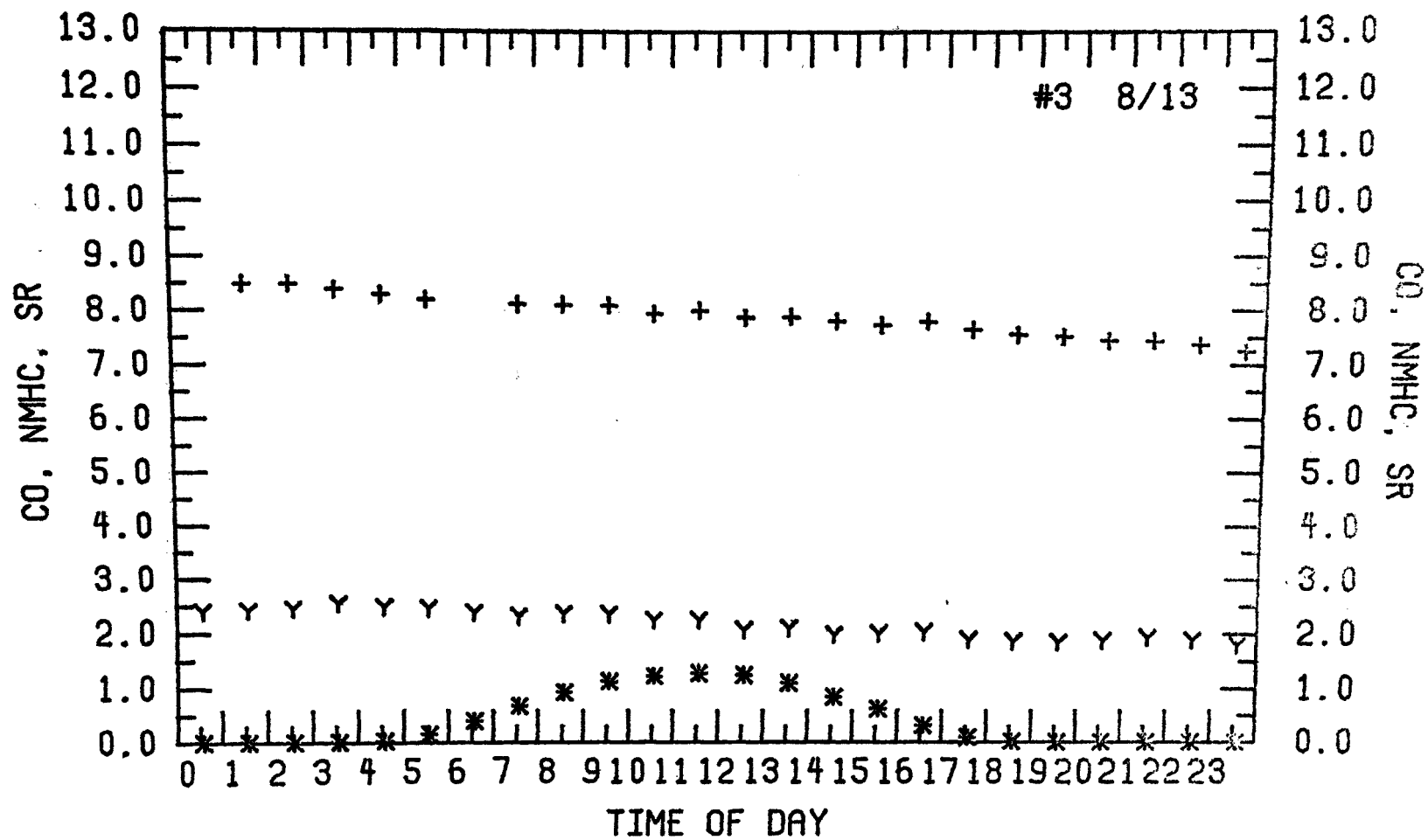




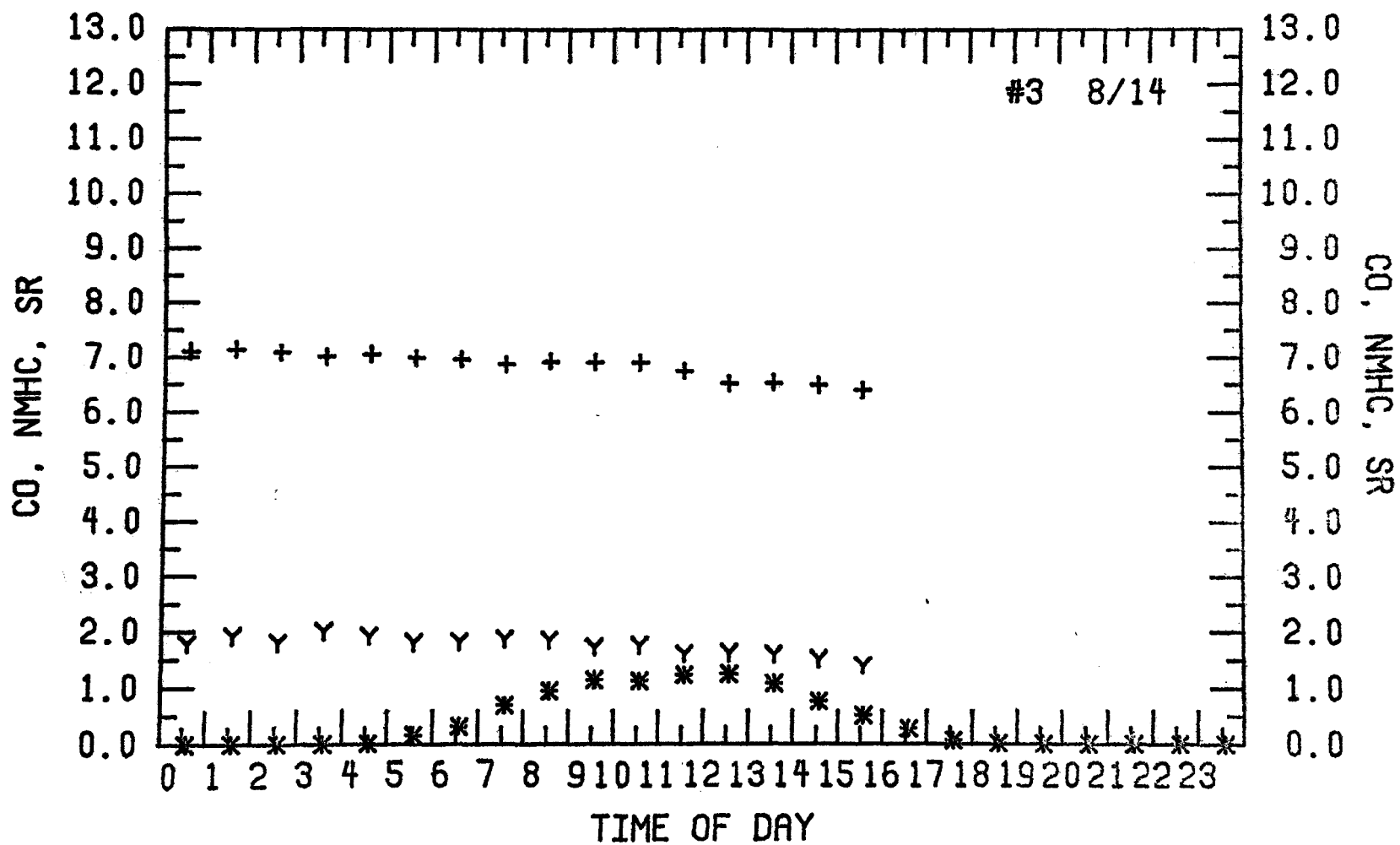


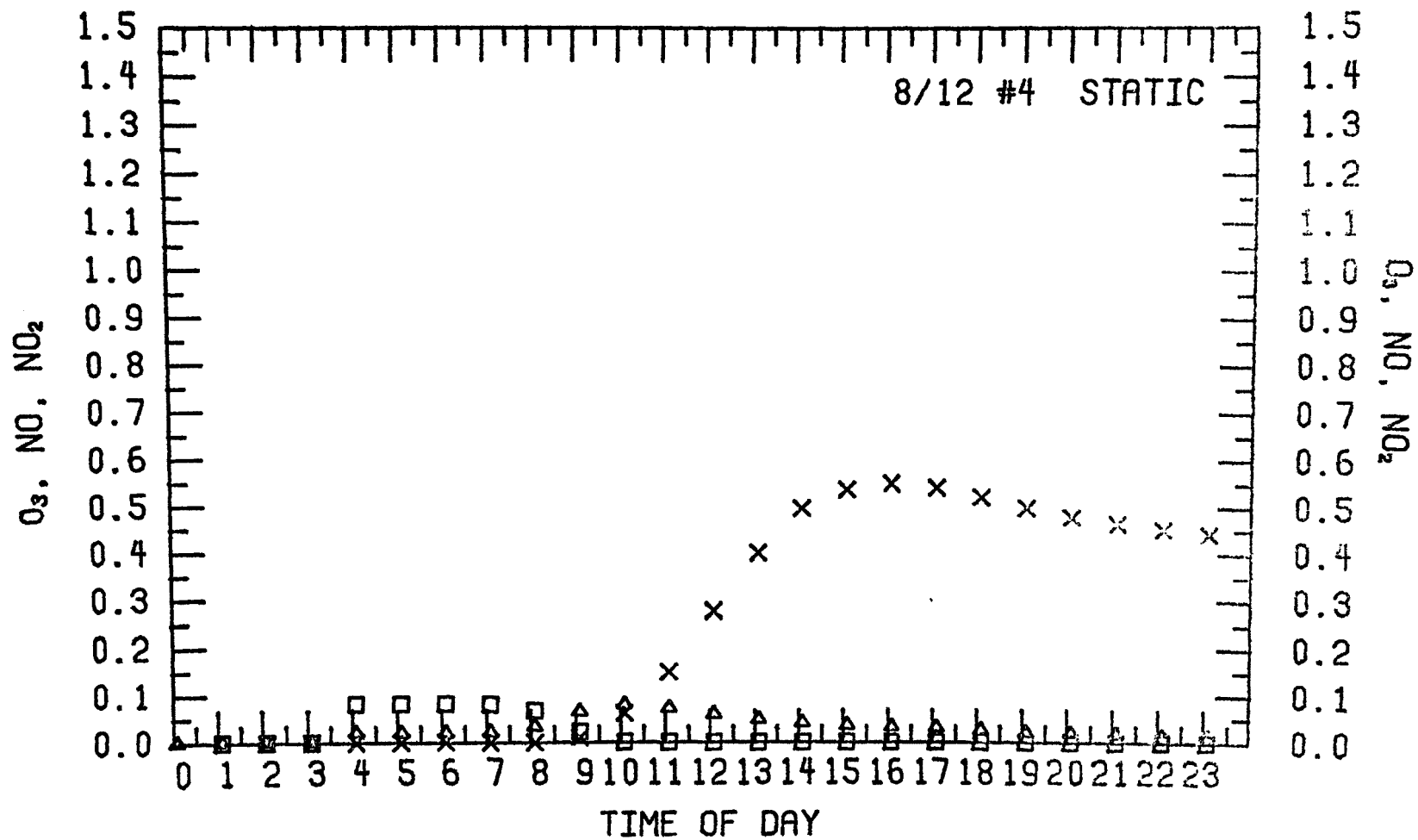


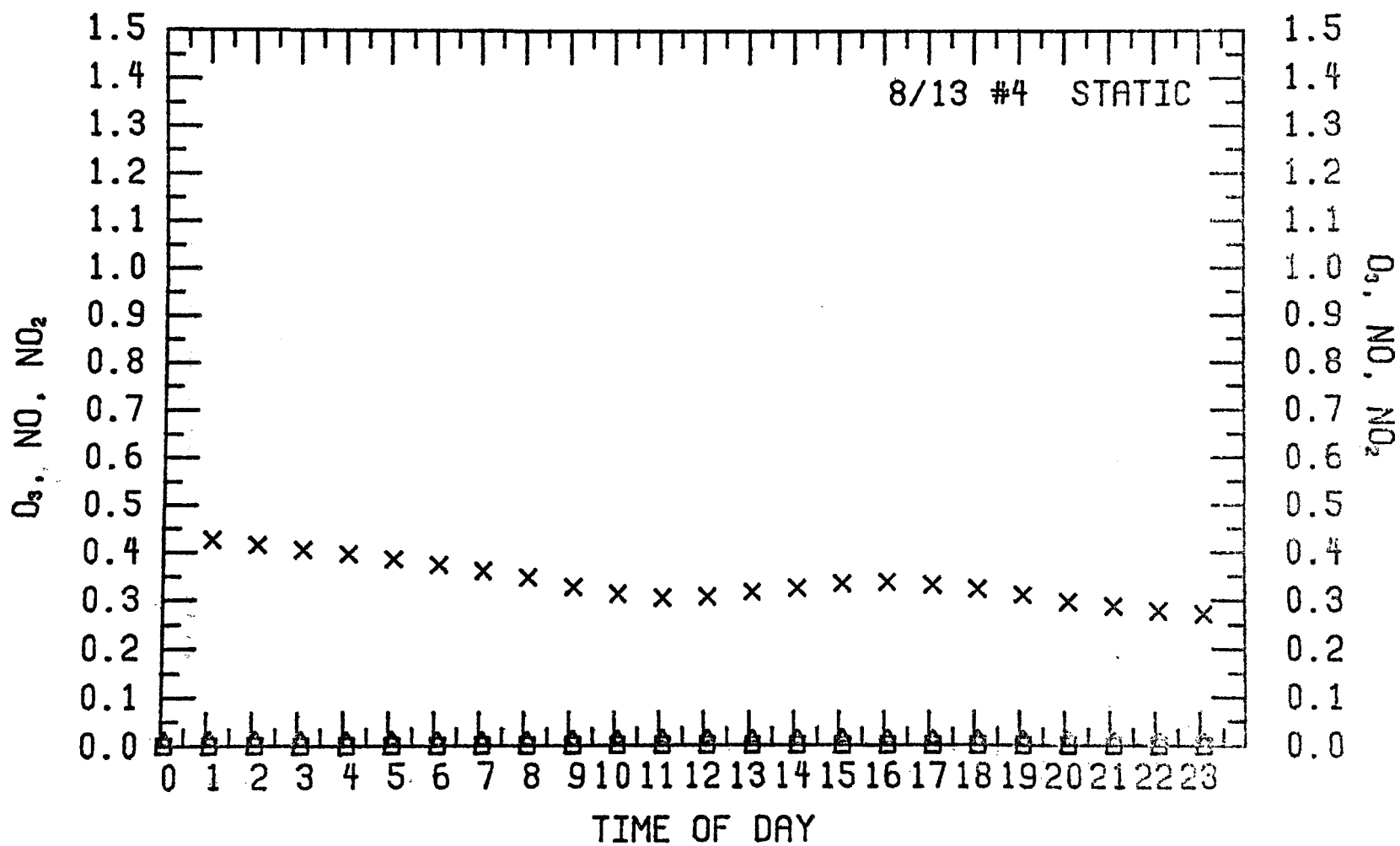


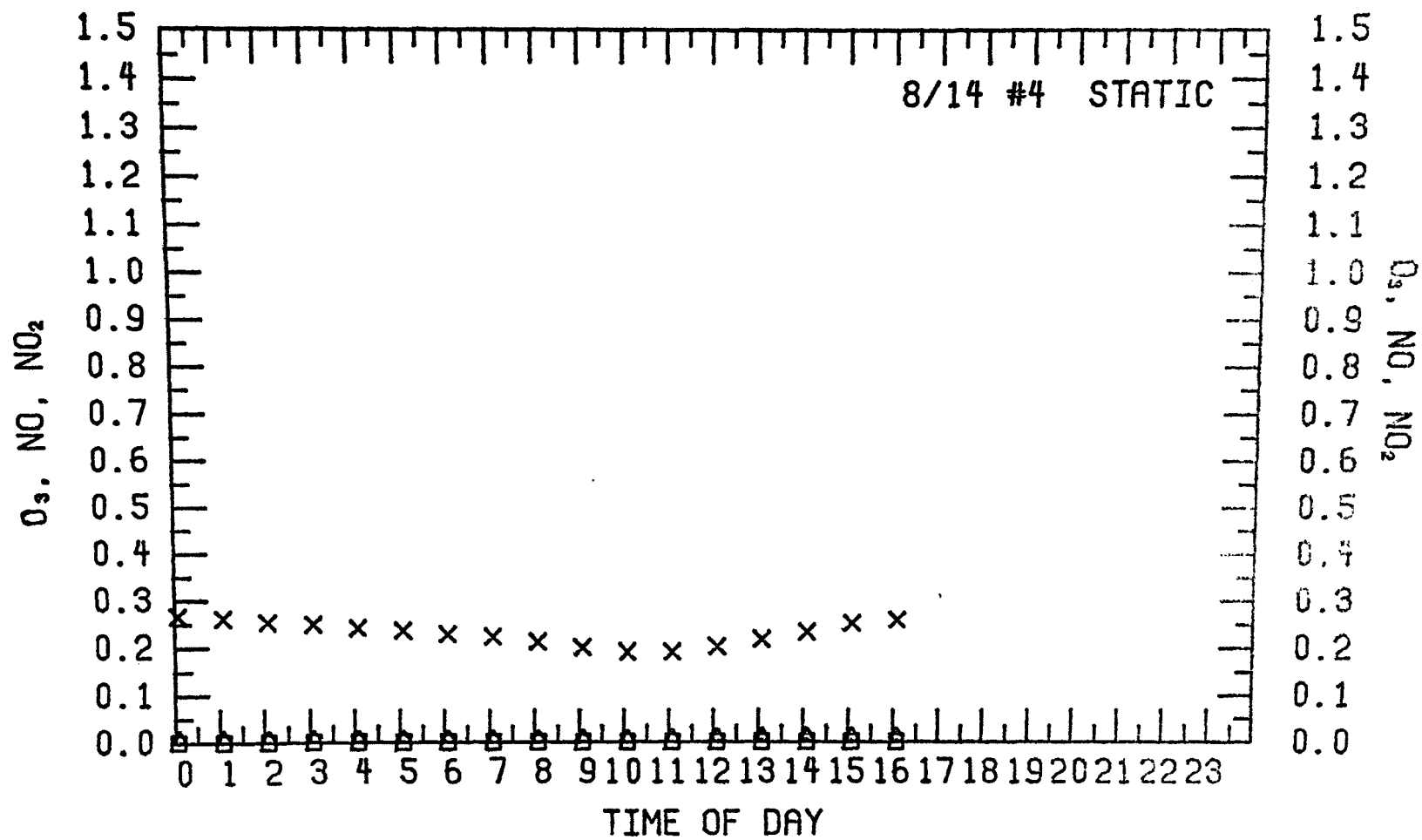


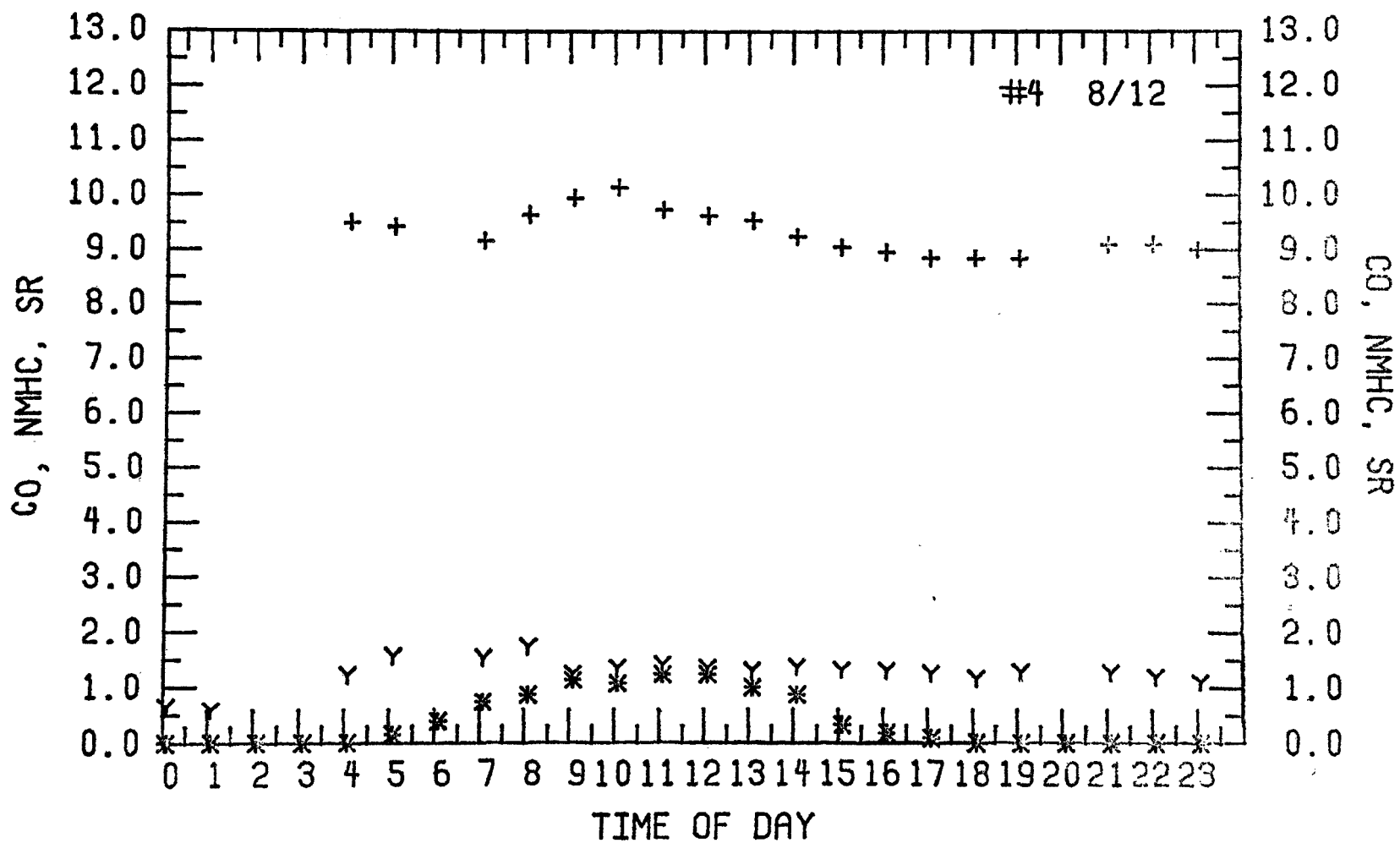


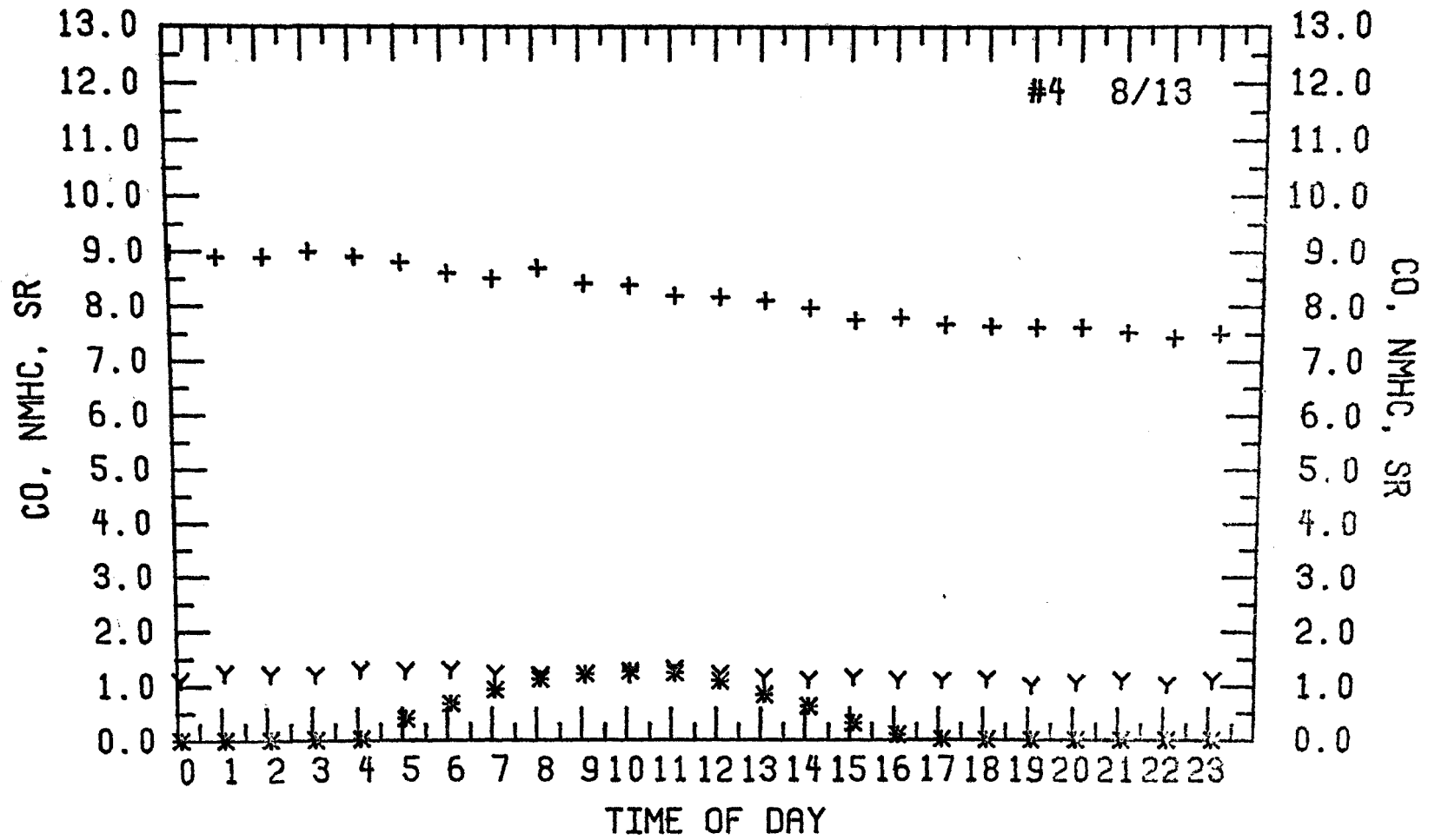


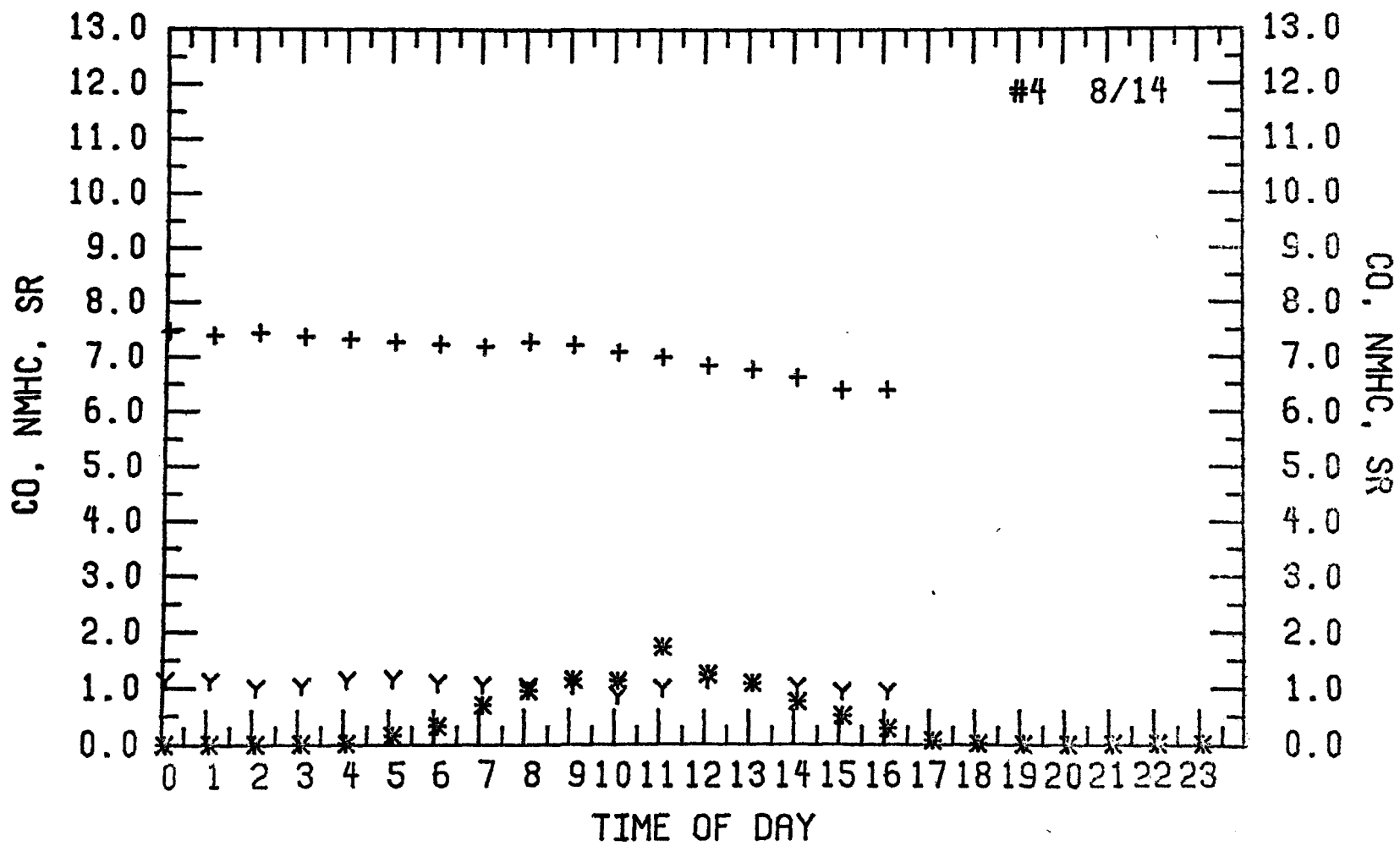












<b>TECHNICAL REPORT DATA</b> <i>(Please read Instructions on the reverse before completing)</i>		
1. REPORT NO. EPA-600/3-76-107	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE OXIDANT-PRECURSOR RELATIONSHIPS DURING POLLUTANT TRANSPORT CONDITIONS An Outdoor Smog Chamber Study		5. REPORT DATE November 1976
7. AUTHOR(S) L. A. Ripperton, J. E. Sickles, II, and W. C. Eaton		6. PERFORMING ORGANIZATION CODE
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute Research Triangle Park, North Carolina 27709		8. PERFORMING ORGANIZATION REPORT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO. 1AA603 (1AA008)
		11. CONTRACT/GRANT NO. 68-02-1296
		13. TYPE OF REPORT AND PERIOD COVERED Final 5/74 - 11/75
		14. SPONSORING AGENCY CODE EPA-ORD
15. SUPPLEMENTARY NOTES		
16. ABSTRACT <p>The formation of ozone under simulated conditions of pollutant transport was studied in a group of four 27-cubic-meter outdoor smog chambers. The chambers were constructed of 5 mil FEP Teflon on aluminum frames. The initial charges in the smog chambers were irradiated for three days by natural sunlight. Simulation of transport was accomplished by progressively diluting the contents of the chambers with clean air.</p> <p>The analogy between the chemical behavior of chamber simulations and nonurban high-ozone (i.e., 0.08 ppm) systems in the field was good. On the second and third days, the initial charges in the chambers generated ozone concentrations greater than the National Ambient Air Quality Standard for photochemical oxidant (0.08 ppm).</p> <p>The initial charge of nonmethane hydrocarbon (NMHC) ranged from 1.0 to 10.0 ppmC; nitrogen oxides (NO<sub>x</sub>) ranged from 0.100 to 1.000 ppm. Therefore, initial ratios of NMHC/NO<sub>x</sub> varied from 7 to 20. On the second and third days in the chambers, concentrations of NO<sub>x</sub> ranged from 0.001 to 0.053 ppm; NMHC ranged from 0.33 to 3.78 ppmC. The resulting NMHC/NO<sub>x</sub> ratios varied from 16 to 610.</p> <p>This report was submitted in fulfillment of EPA contract 68-02-1296 (43U-994, RTI Contract Number) by the Research Triangle Institute under the sponsorship of the Environmental Protection Agency.</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution      Chemical analysis		13B
* Ozone		07B
* Nitrogen oxides		07C
* Aliphatic hydrocarbons		14B
* Test chambers		03B
Solar radiation		07E
* Photochemical reactions		07D
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 223
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE



## INSTRUCTIONS

- 1. REPORT NUMBER**  
Insert the EPA report number as it appears on the cover of the publication.
- 2. LEAVE BLANK**
- 3. RECIPIENTS ACCESSION NUMBER**  
Reserved for use by each report recipient.
- 4. TITLE AND SUBTITLE**  
Title should indicate clearly and briefly the subject coverage of the report, and be displayed prominently. Set subtitle, if used, in smaller type or otherwise subordinate it to main title. When a report is prepared in more than one volume, repeat the primary title, add volume number and include subtitle for the specific title.
- 5. REPORT DATE**  
Each report shall carry a date indicating at least month and year. Indicate the basis on which it was selected (*e.g., date of issue, date of approval, date of preparation, etc.*).
- 6. PERFORMING ORGANIZATION CODE**  
Leave blank.
- 7. AUTHOR(S)**  
Give name(s) in conventional order (*John R. Doe, J. Robert Doe, etc.*). List author's affiliation if it differs from the performing organization.
- 8. PERFORMING ORGANIZATION REPORT NUMBER**  
Insert if performing organization wishes to assign this number.
- 9. PERFORMING ORGANIZATION NAME AND ADDRESS**  
Give name, street, city, state, and ZIP code. List no more than two levels of an organizational hierarchy.
- 10. PROGRAM ELEMENT NUMBER**  
Use the program element number under which the report was prepared. Subordinate numbers may be included in parentheses.
- 11. CONTRACT/GRANT NUMBER**  
Insert contract or grant number under which report was prepared.
- 12. SPONSORING AGENCY NAME AND ADDRESS**  
Include ZIP code.
- 13. TYPE OF REPORT AND PERIOD COVERED**  
Indicate interim final, etc., and if applicable, dates covered.
- 14. SPONSORING AGENCY CODE**  
Leave blank.
- 15. SUPPLEMENTARY NOTES**  
Enter information not included elsewhere but useful, such as: Prepared in cooperation with, Translation of, Presented at conference of, To be published in, Supersedes, Supplements, etc.
- 16. ABSTRACT**  
Include a brief (*200 words or less*) factual summary of the most significant information contained in the report. If the report contains a significant bibliography or literature survey, mention it here.
- 17. KEY WORDS AND DOCUMENT ANALYSIS**
  - (a) **DESCRIPTORS** - Select from the Thesaurus of Engineering and Scientific Terms the proper authorized terms that identify the major concept of the research and are sufficiently specific and precise to be used as index entries for cataloging.
  - (b) **IDENTIFIERS AND OPEN-ENDED TERMS** - Use identifiers for project names, code names, equipment designators, etc. Use open-ended terms written in descriptor form for those subjects for which no descriptor exists.
  - (c) **COSATI FIELD GROUP** - Field and group assignments are to be taken from the 1965 COSATI Subject Category List. Since the majority of documents are multidisciplinary in nature, the Primary Field/Group assignment(s) will be specific discipline, area of human endeavor, or type of physical object. The application(s) will be cross-referenced with secondary Field/Group assignments that will follow the primary posting(s).
- 18. DISTRIBUTION STATEMENT**  
Denote releasability to the public or limitation for reasons other than security for example "Release Unlimited." Cite any availability to the public, with address and price.
- 19. & 20. SECURITY CLASSIFICATION**  
DO NOT submit classified reports to the National Technical Information service.
- 21. NUMBER OF PAGES**  
Insert the total number of pages, including this one and unnumbered pages, but exclude distribution list, if any.
- 22. PRICE**  
Insert the price set by the National Technical Information Service or the Government Printing Office, if known.